Diastereodivergent Combined Carbometalation/Zinc Homologation/C-C Fragmentation Reaction as an Efficient Tool to Prepare Acyclic Allylic Quaternary Carbon Stereocenters

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General Considerations:

All glassware was flame dried under vacuum, and cooled under argon prior to use. Unless otherwise stated, all reactions were carried out under positive pressure of argon. Ether and THF were dried from Pure-Solv® Purification System (Innovative Technology©). Dichloromethane was distilled from CaH_2. Toluene was distilled from sodium and benzophenone. Copper iodide, rhodium acetate dimer, methyllithium (1.6 M in diethyl ether), butyllithium (1.6 M in hexane), hexyllithium (2.3 M in hexane), phenyllithium (1.9 M in dibutyl ether), methylmagnesium bromide (3.0 M in diethyl ether), vinylmagnesium bromide (1.0 M in THF) and diethylzinc (1 M in hexane) were purchased from Aldrich. Thin Layer Chromatography (TLC) was performed using Merck© silica gel 60 F254 plates and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, phosphomolybdic acid, or potassium permanganate. Column chromatography was performed using Bio-Lab silica gel 60A (0.040-0.063mm). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker© spectrometers AVIII400, using $CDCl_3$ as a solvent. NMR data were processed with *Topspin* or with *NMRnotebook*. Peak multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m= multiplet. GC-MS was performed on Thermo Scientific™ Ion Trap GC/MS: ITQTM 900 with a Varian Factor Four Capilary colum (VF-5 ms, 30 m × 0.25 mm). HPLC chromatograms were recorded using Agilent© 1100 Series line with CHIRALPAK® AD-H, AY-H, IA or CHIRALCEL® OD columns. Optical rotation were measured using SCHMIDT and HAENSCH© Unipol L1000 with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL.

Experimental section:

Synthesis of benzyl 2-diazoacetate:

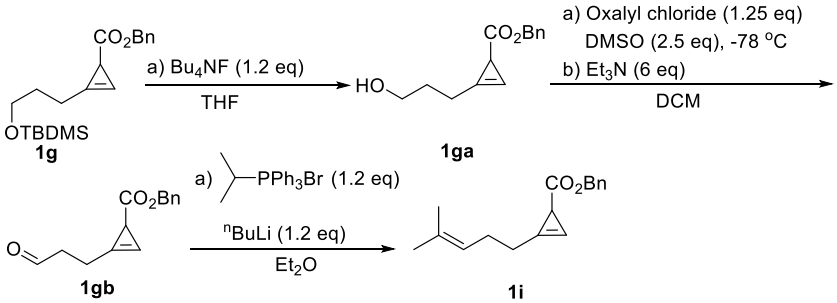
The benzyl 2-diazoacetate was synthesized from benzyl acetoacetate by following the reported procedure.[1]

General procedure for the preparation of cyclopropene carboxylates:

Following the reported procedure[2] cyclopropene carboxylates were prepared from the reaction of alkyne[3] and alkyl 2-diazoacetate.

Synthesis of benzyl 2-(4-methylpent-3-en-1-yl)cycloprop-2-ene-1-carboxylate (1i):

Title compound was synthesized following the reported procedures as mentioned in the following scheme.



[1] H. Mao, A. Lin, Y. Shi, Z. Mao, X. Zhu, W. Li, H. Hu, Y. Cheng and C. Zhu, *Angew. Chem. Int. Ed.*, 2013, **52**, 6288.

[2] L.-A. Liao, F. Zhang, N. Yan, J. A. Golen and J. M. Fox, *Tetrahedron* 2004, **60**, 1803.

[3] All alkynes were commercially available except *tert*-butyldimethyl(pent-4-yn-1-yloxy)silane which was prepared according to the reported procedure (L. Cleary, H. Yoo and K. J. She, *Org. Lett.*, 2011, **7**, 1781).

Then Swern oxidation was performed with **1ga**. Oxalyl chloride (1.25 eq, 0.54 mL, 6.25 mmol) was dissolved in 20 mL of DCM and kept at -78 ^{o}C. Then DMSO (2.5 eq, 0.89 mL, 12.5 mmol; solution was prepared in 5 mL DCM) was added dropwise and stirred for 30 min. Then **1ga** (1 eq, 1.16 g, 5 mmol; solution was prepared in 5 mL DCM) was added and stirred for 1h. Then triethlyamine (6 eq, 4.1 mL, 30 mmol) was added and stirred overnight. The mixture was then diluted with 20 mL DCM and poured over 10 mL of a saturated aqueous solution of NH_4Cl. The organic layer was separated and dried over Na_2SO_4 and concentrated in vacuum to yield a crude oil which was further purified by flash column chromatography (hexane/ EtOAc, 99:1) to get **1gb** in 95% yield (1.1 g).

Finally the Wittig reaction was performed with **1gb** to get the title compound. Isopropyl triphenylphosphonium bromide salt was prepared separately from the reaction of triphenylphosphine and 2-bromopropane.[4b] To a cooled mixture (0 °C) of isopropyltriphenylphosphonium bromide (1.2 eq, 927 mg, 2.4 mmol) in 10 mL of dry Et_2O (ca. 10 mL) was added ^{n}BuLi (1.2 eq, 2.4 mmol, 1.6 M in hexane) under inert atmosphere. The solution turned red due to the formation of the corresponding ylide. After the mixture was stirred for 1 h at room temperature, a solution of the aldehyde **1gb** (1 eq, 461 mg, 2 mmol) in 5 mL of dry Et_2O was added dropwise and stirring was continued at room temperature. The reaction mixture was monitored by TLC. After completion of the reaction hexane was added to the reaction mixture to precipitate the triphenylphosphine oxide (Ph_3PO). After filtration, the solution was concentrated, and the residue was purified by flash column chromatography (hexane/ EtOAc, 99:1) to get the compound **1i** in 62% yield (320 mg).

Synthesis of enantioenricheded cyclopropene:

$Rh_2(OAc)(R,R\text{-DPTI})_3$ (DPTI = diphenyltriflylimidazolidinone) which was prepared following the reported procedure[4], was used as a chiral catalyst for the synthesis of enantioenriched cyclopropene.

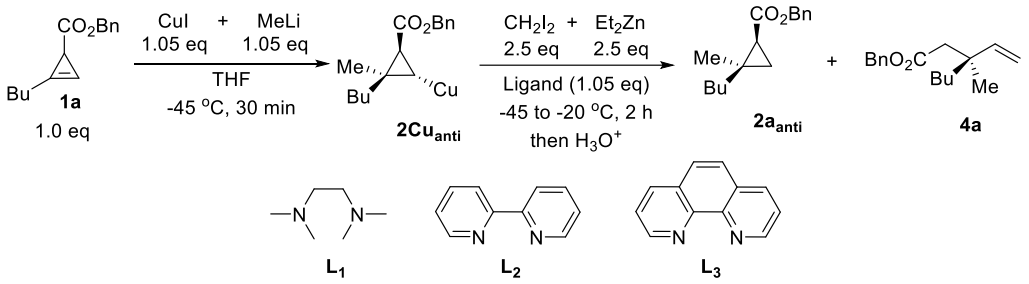
To a flame dried 3-necked 100ml round bottom flask equipped with a Teflon stirring bar under argon atmosphere $Rh_2(OAc)(R,R\text{-DPTI})_3$ (0.5 mol%, 6.86 mg) was added and dissolved in 9 mL of dry DCM, followed by the addition of alkyne (10 eq, 10 mmol). Then a solution of methyl 2-diazo-2-phenylacetate (1 mmol in 7 ml DCM) was added to the reaction mixture through a syringe pump with 0.5 mL/h flow rate. The reaction was followed by TLC until disappearance of alkyl 2-diazoacetate (eluent hexane/EtOAc, 9:1). The solvent was evaporated and the resulting mixture purified by column chromatography (hexane/ EtOAc, 95:5) to afford the enantioenricheded cyclopropene product as clear color less oil. Following this procedure all the enantioenricheded cyclopropene **1b**, **1e** and **1f** were synthesized.

The absolute configuration of the **1f** was determined by comparing the optical rotation described in the literature with an authentic sample after reduction into the corresponding alcohol with DIBAL.[2] Characterization and spectral data of the alcohol was compatible with literature data.[5] The absolute configuration of the **1b** and **1e** was assumed to be the same of the analogous **1f**.

[4] Y. Lou, M. Horikawa, R. A. Kloster, N. A. Hawryluk and E. J. Corey, *J. Am. Chem. Soc*. 2004, **126**, 8916.
[5] L.-A. Liao and J. M. Fox, *J. Am. Chem. Soc*., 2002, **124**, 14322.

Optimization of reaction conditions:

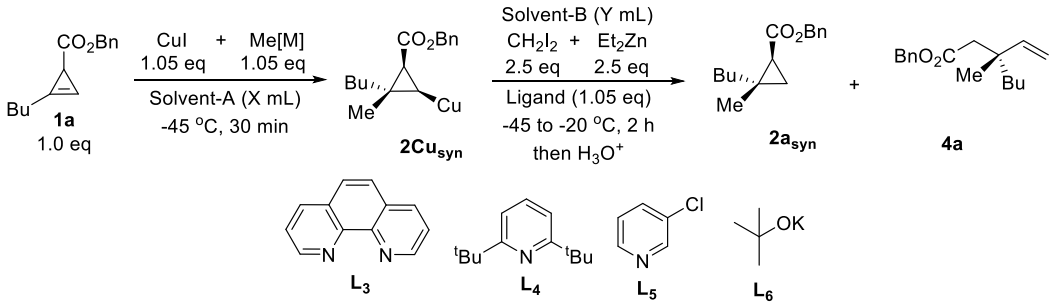
Table S-1: Combined **anti**-carbometalation − zinc homologation – fragmentation reactions



Entry	Ligand	$2a_{anti}$ /4a[a]
1	---	27:73
2	L_1	12:88
3	L_2	13:87
4	**L_3**	**06:94 (72)**

[a] **1a** was consumed completely and the ratio between products **$2a_{anti}$** and **4a** was determined by GC-MS of the crude reaction mixture. Parentheses represent isolated yield after purification by column chromatography.

Table S-2: Combined **syn**-carbometalation − zinc homologation – fragmentation reactions



Entry	Me[M]	Solvent-A	Solvent-B	X:Y	Ligand	$2a_{syn}$ /4a[a]
1	MeLi	PhMe	---	---	L_3	67:33
2	MeLi	PhMe	THF	1:1	L_3	61:39
3	MeLi	PhMe	THF	1:2	L_3	45:55
4	MeMgBr	Et_2O	THF	1:2	L_3	73:27
5	MeMgBr	PhMe	THF	1:2	L_3	80:20
6	MeLi	PhMe	THF	1:2	L_4	88:12
7	MeLi	PhMe	THF	1:2	L_5	60:40
8	**MeLi**	**PhMe**	**THF**	**1:2**	**L_6**	**11:89 (65)**
9	MeLi	PhMe	THF	1:2	--	80:20

[a] **1a** was consumed completely and ratio between products **$2a_{syn}$** and **4a** was determined by GC-MS of the crude reaction mixture. Parentheses represent isolated yield after purification by column chromatography.

Procedure for the synthesis of $2a_{anti}$:

To a suspension of CuI (100 mg, 1.05 equiv, 0.525 mmol) in 6 mL of THF, MeLi was added drop-wise at -45 ^{o}C (1.05 equiv, 0.525 mmol). The reaction mixture was allowed to stir for 30 min after which the **1a** (1 equiv, 115 mg, 0.5 mmol, dissolved in 2 ml of THF) was added drop-wise at that temperature and the reaction mixture was stirred until TLC shows complete consumption of the starting cyclopropene (eluant Hexane:Et_2O = 95:5 ca. 30 min). The reaction was then quenched with an aqueous solution of NH_4Cl/NH_4OH (2:1). The aqueous layer was extracted twice with Et_2O and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude mixtures were then purified by flash chromatography using hexane/ Et_2O as eluent to get the compound $\mathbf{2a_{anti}}$ in 75% yield (93 mg).

Procedure for the synthesis of $2a_{syn}$:

To a suspension of CuI (100 mg, 1.05 equiv, 0.525 mmol) in 6 mL of PhMe, MeLi was added drop-wise at -45 ^{o}C (1.05 equiv, 0.525 mmol). The reaction mixture was allowed to stir for 30 min after which the **1a** (1 equiv, 115 mg, 0.5 mmol, dissolved in 2 ml of PhMe) was added drop-wise at that temperature and the reaction mixture was stirred until TLC shows complete consumption of the starting cyclopropene (eluent Hexane:Et_2O = 95:5 ca. 30 min). The reaction was then quenched with an aqueous solution of NH_4Cl/NH_4OH (2:1). The aqueous layer was extracted twice with Et_2O and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude mixtures were then purified by flash chromatography using hexane/ Et_2O as eluent to get the compound $\mathbf{2a_{syn}}$ in 72% yield (90 mg).

General procedure for anti-Carbometalation/Zinc-Homologation/Ring opening of cyclopropanes:

To a suspension of CuI (0.1 g, 1.05 equiv, 0.525 mmol) in 8 mL of THF, alkyllithium was added drop-wise at -45 ^{o}C (1.05 equiv, 0.525 mmol). The reaction mixture was allowed to stir for 30 min after which the cyclopropene (1 equiv, 0.5 mmol, dissolved in 2 ml of THF) was added drop-wise at that temperature and the reaction mixture was stirred until TLC shows complete consumption of the starting cyclopropene (eluent Hexane:Et_2O = 95:5 ca. 30 min). Then, to the reaction mixture CH_2I_2 (0.1 mL, 2.5 equiv, 1.25 mmol) was added followed by the drop-wise addition of Et_2Zn (2.5 equiv, 1.25 mmol) and 1,10-phenanthroline (0.095 g, 1.05 equiv, 0.525 mmol, dissolved in 3 ml of THF). The resulting reacting mixture (dark yellow to brown in case of MeLi) was stirred at this temperature and slowly warmed up to -20 ^{o}C (ca. 2h). The reaction was then quenched with an aqueous solution of NH_4Cl/NH_4OH (2:1). The aqueous layer was extracted twice with Et_2O and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude mixtures were then purified by flash chromatography using hexane/ Et_2O as eluent.

General procedure for syn-Carbometalation/Zinc-Homologation/Ring opening of cyclopropanes:

To a suspension of CuI (0.1 g, 1.05 equiv, 0.525 mmol) in 6 mL of PhMe, alkyllithium was added drop-wise at -45 ^{o}C (1.05 equiv, 0.525 mmol). The reaction mixture was allowed to stir for 30 min after which the cyclopropene (1 equiv, 0.5 mmol, dissolved in 2 ml of PhMe) was added drop-wise at that temperature and the reaction mixture was stirred until TLC shows complete consumption of the starting cyclopropene (eluent Hexane:Et_2O = 95:5 ca. 30 min). Then to that reaction mixture THF (16 mL) and CH_2I_2 (0.1 mL, 2.5 equiv, 1.25 mmol) was added followed by the drop-wise addition of Et_2Zn (2.5 equiv, 1.25 mmol) and 1,10-phenanthroline (0.095 g, 1.05 equiv, 0.525 mmol, dissolved in 3 ml of THF). The resulting reacting mixture (dark yellow to brown in case of MeLi) was stirred at this temperature and slowly warmed up to -20 ^{o}C (ca. 2h). The reaction was then quenched with an aqueous solution of

NH_4Cl/NH_4OH (2:1). The aqueous layer was extracted twice with Et_2O and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crude mixtures were then purified by flash chromatography using hexane/ Et_2O as eluent.

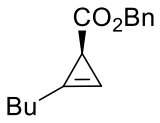
General procedure for the ozonolysis of 4b, **4g**, **4h** and **4i:**

The determination of the enantiomeric excess of **4b**, **4g**, **4h** and **4i** could not be done by HPLC with CHIRALPAK® AD-H , AY-H, IA or CHIRALCEL® OD columns. Therefore ozonolysis was performed on the **4b**, **4g**, **4h** and **4i** to convert them into the corresponding aldehyde **5b**, **5g**, **5h** and **5i**.

4 (1 eq, 0.25 mmol) was dissolved in 7 mL of DCM and kept at -78 °C. Then ozone was purged to the solution until reaction mixture turn into pale blue colour (ca. 5 min). Triphenylphosphine (4 eq, 262 mg, 1 mmol) was added at a time and kept at that temperature for 30 min then at rt for 12h. The mixture was then concentrated in vacuo and further purified by flash column chromatography (hexane/ EtOAc, 90:10) to get the desired **5**.

Characterization of starting materials:

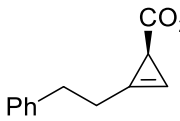
Benzyl 2-butylcycloprop-2-ene-1-carboxylate (1a):



R_f = 0.57 (Hexane/Et_2O = 94:6); Yield: 65% (Colorless oil)

^1H NMR (400 MHz, $CDCl_3$): 0.90 (t, *J* = 7.2 Hz, 3H), 1.33-1.42 (m, 2H), 1.52-1.65 (m, 2H), 2.19 (d, *J* = 1.2 Hz, 1H), 2.48-2.51 (m, 2H), 5.10 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 6.33 (d, *J* = 1.2 Hz, 1H), 7.30-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 19.7, 22.2, 24.7, 28.7, 66.0, 93.8, 115.5, 128.0, 128.1, 128.5, 136.5, 176.5; HRMS (ESI) calcd. for $C_{15}H_{18}NaO_2$ $[M+Na]^+$: 253.1240; found: 253.1199

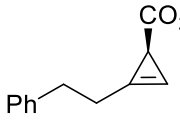
Benzyl 2-phenethylcycloprop-2-ene-1-carboxylate (1b):



R_f = 0.43 (Hexane/Et_2O = 94:6); Yield: 62% (Colorless oil)

^1H NMR (400 MHz, $CDCl_3$): δ = 2.04 (d, *J* = 1.2 Hz, 1H), 2.63-2.76 (m, 4H), 4.93 (d, *J* = 12.4 Hz, 1H), 4.98 (d, *J* = 12.4 Hz, 1H), 6.20 (d, *J* = 1.2 Hz, 1H), 7.02-7.06 (m, 3H), 7.09-7.12 (m, 2H), 7.14-7.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 26.7, 32.9, 66.1, 94.9, 114.8, 126.3, 128.0, 128.1, 128.3, 128.4, 128.5, 136.4, 140.6, 176.2; HRMS (ESI) calcd. for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1385; found: 279.1350.

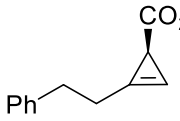
(*S*)-Benzyl 2-phenethylcycloprop-2-ene-1-carboxylate ((*S*)-1b):



R_f = 0.43 (Hexane/Et_2O = 94:6); Yield: 80% (Colorless oil)

Spectral data of the title compound were identical to the racemic sample. e.r. = 96:4. The chiral sample was analyzed by HPLC using a CHIRALPAK® IA column (4.6mmØ×250mmL), n-hexane/isopropanol 99:1, 1mL/min, 210nm. t_R (major) = 10.78 min, t_R (minor) = 12.12 min. $[\alpha]_D$: ($CHCl_3$, c = 0.40): 24.55°.

Ethyl 2-phenethylcycloprop-2-ene-1-carboxylate[6] (1c):

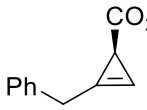


R_f = 0.52 (Hexane/Et_2O = 94:6); Yield: 60% (Colorless oil)

^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.2 Hz, 3H), 2.14 (d, *J* = 1.2 Hz, 1H), 2.79-2.84 (m, 2H), 2.88-2.93 (m, 2H), 4.08-4.17 (m, 2H), 6.35 (d, *J* = 1.2 Hz, 1H), 7.19-7.22 (m, 3H), 7.25-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 19.9, 26.8, 32.9, 60.2, 94.9, 114.9, 126.2, 128.3, 128.4, 140.7, 176.4; HRMS (ESI) calcd. for $C_{14}H_{17}O_2$ $[M+H]^+$: 217.1262; found: 217.1223.

[6] F.-G. Zhang, G. Eppe and I. Marek, *Angew.Chem. Int. Ed*., 2016, **55**, 714.

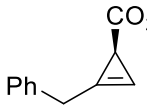
Ethyl 2-benzylcycloprop-2-ene-1-carboxylate[7] (1d):



R_f = 0.52 (Hexane/Et_2O = 94:6); Yield: 61% (Colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (t, *J* = 7.2 Hz, 3H), 2.15 (d, *J* = 1.6 Hz, 1H), 3.77 (q, *J* = 17.6 Hz, 2H), 3.98-4.04 (m, 2H), 6.39 (d, *J* = 1.2 Hz, 1H), 7.15-7.19 (m, 3H), 7.22-7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 20.6, 31.6, 60.4, 95.8, 114.8, 126.9, 128.8 (x2), 136.4, 176.2; HRMS (ESI) calcd. for $C_{13}H_{14}NaO_2$ $[M+Na]^+$: 225.0932; found: 225.0886.

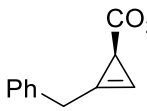
Benzyl 2-benzylcycloprop-2-ene-1-carboxylate (1e):



R_f = 0.51 (Hexane/Et_2O = 95:5); Yield: 63% (Colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): 2.25 (d, *J* = 1.6 Hz, 1H), 3.74 (d, *J* = 17.6 Hz, 1H), 3.84 (d, *J* = 17.6 Hz, 1H), 5.04 (s, 2H), 6.43 (d, *J* = 1.2 Hz, 1H), 7.19-7.24 (m, 3H), 7.25-7.32 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4, 31.4, 66.1, 95.6, 114.5, 126.8, 128.05, 128.09, 128.5, 128.6, 128.7, 136.1, 136.6, 175.9; HRMS (ESI) calcd. for $C_{18}H_{17}O_2$ $[M+H]^+$: 265.1287; found: 265.1223.

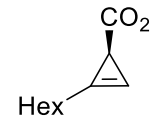
(*S*)-Benzyl 2-benzylcycloprop-2-ene-1-carboxylate ((*S*)-1e):



R_f = 0.51 (Hexane/Et_2O = 95:5); Yield: 80% (Colorless oil)

Spectral data of the title compound were identical to the racemic sample. e.r. = 93:7. The chiral sample was analyzed by HPLC using a CHIRALCEL® OD column (4.6mmØ×250mmL), n-hexane/isopropanol 99:1, 1 mL/min, 210nm. t_R (major) = 16.53 min, t_R (minor) = 14.98 min. $[\alpha]_D$: ($CHCl_3$, c = 0.30): 3.64°.

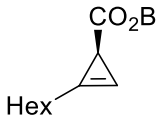
Benzyl 2-hexylcycloprop-2-ene-1-carboxylate (1f):



R_f = 0.62 (Hexane/Et_2O = 94:6); Yield: 64% (Colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (t, *J* = 7.2 Hz, 3H), 1.24-1.36 (m, 6H), 1.52-1.58 (m, 2H), 2.19 (d, *J* = 1.2 Hz, 1H), 2.46-2.50 (m, 2H), 5.09 (d, *J* = 12.8 Hz, 1H), 5.14 (d, *J* = 12.8 Hz, 1H), 6.33 (d, *J* = 1.2 Hz, 1H), 7.31-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 19.7, 22.5, 24.9, 26.6, 28.8, 31.5, 66.0, 93.8, 115.6, 128.0, 128.1, 128.5, 136.5, 176.5; HRMS (ESI) calcd. for $C_{17}H_{22}NaO_2$ $[M+Na]^+$: 281.1563; found: 281.1512.

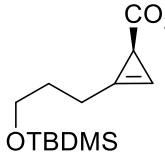
(*S*)-Benzyl 2-hexylcycloprop-2-ene-1-carboxylate ((*S*)-1f):



R_f = 0.62 (Hexane/Et_2O = 94:6); Yield: 82% (Pale pellow oil)

Spectral data of the title compound were identical to the racemic sample. e.r. = 91:9. The chiral sample was analyzed by HPLC using a CHIRALPAK® IA column (4.6mmØ×250mmL), n-hexane/isopropanol 99:1, 1 mL/min, 210 nm. t_R (major) = 6.30 min, t_R (minor) = 6.76 min. $[\alpha]_D$: ($CHCl_3$, c = 0.42): 12.08°.

Benzyl 2-(3-((*tert*-butyldimethylsilyl)oxy)propyl)cycloprop-2-ene-1-carboxylate (1g):

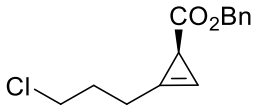


R_f = 0.67 (Hexane/Et_2O = 95:5); Yield: 65% (Colorless oil)

^{1}H NMR (400 MHz, $CDCl_3$): 0.03 (s, 6H), 0.88 (s, 9H), 1.74-1.81 (m, 2H), 2.19 (d, *J* = 1.2 Hz, 1H), 2.57 (t, *J* = 7.2 Hz, 2H), 3.61-3.65 (m, 2H), 5.09 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 6.35 (d, *J* = 1.2 Hz, 1H), 7.28-7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = -5.3 (x2), 18.3, 19.8, 21.5, 25.9 (x3), 29.8, 61.9, 66.0, 94.2, 115.2, 128.0, 128.1, 128.5, 136.4, 176.4; HRMS (ESI) calcd. for $C_{20}H_{31}O_3Si$ $[M+H]^+$: 347.1968; found: 347.2037.

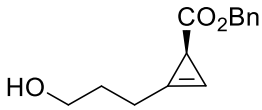
[7] P. -O. Delaye, D. Didier and I. Marek, *Angew. Chem. Int. Ed*., 2013, **52**, 5333.

Benzyl 2-(3-chloropropyl)cycloprop-2-ene-1-carboxylate (1h):



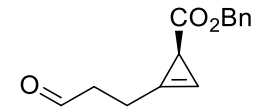
R_f = 0.47 (Hexane/Et_2O = 95:5); Yield: 63% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): 2.00-2.06 (m, 2H), 2.22 (d, *J* = 1.6 Hz, 1H), 2.66-2.71 (m, 2H), 3.53-3.60 (m, 2H), 5.09 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 6.44 (d, *J* = 1.6 Hz, 1H), 7.30-7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 22.4, 29.6, 43.8, 66.2, 95.4, 114.1, 128.1, 128.2, 128.5, 136.3, 176.1; HRMS (ESI) calcd. for $C_{14}H_{15}ClNaO_2$ $[M+Na]^+$: 273.0806; found: 273.0659.

Benzyl 2-(3-oxopropyl)cycloprop-2-ene-1-carboxylate (1ga):



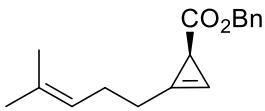
R_f = 0.21 (Hexane/Et_2O = 90:10); Yield: 93% (Pale yellow oil)
^{1}H NMR (400 MHz, $CDCl_3$): 1.75 (t, *J* = 5.6 Hz, 1H), 1.79-1.86 (m, 2H), 2.21 (d, *J* = 1.2 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 3.66-3.70 (m, 2H), 5.09 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 6.38 (d, *J* = 1.6 Hz, 1H), 7.30-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 21.6, 29.5, 61.7, 66.2, 94.7, 114.8, 128.1, 128.2, 128.5, 136.3, 176.6.

Benzyl 2-(3-oxopropyl)cycloprop-2-ene-1-carboxylate (1gb):



R_f = 0.63 (Hexane/Et_2O = 90:10); Yield: 95% (Pale yellow oil)
^{1}H NMR (400 MHz, $CDCl_3$): 2.22 (d, *J* = 1.6 Hz, 1H), 2.70-2.73 (m, 2H), 2.80-2.85 (m, 2H), 5.09 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 6.43 (d, *J* = 1.6 Hz, 1H), 7.31-7.36 (m, 5H), 9.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 19.9, 40.7, 66.2, 95.6, 113.9, 128.1, 128.2, 128.5, 136.2, 175.9, 200.1.

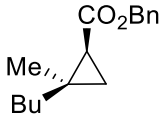
Benzyl 2-(4-methylpent-3-en-1-yl)cycloprop-2-ene-1-carboxylate (1i):



R_f = 0.47 (Hexane/Et_2O = 95:5); Yield: 62% (Pale yellow oil)
^{1}H NMR (400 MHz, $CDCl_3$): 1.60 (s, 3H), 1.67 (s, 3H), 2.19 (d, *J* = 1.6 Hz, 1H), 2.23-2.28 (m, 2H), 2.49-2.54 (m, 2H), 5.08-5.16 (m, 3H), 6.35 (d, *J* = 1.6 Hz, 1H), 7.29-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.7, 19.8, 25.3, 25.7, 66.0, 94.2, 115.3, 122.8, 128.0, 128.1, 128.5, 132.9, 136.5, 176.4; HRMS (ESI) calcd. for $C_{17}H_{21}O_2$ $[M+H]^+$: 257.1481; found: 257.1536.

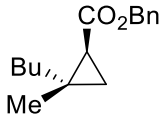
Characterization of compounds:

Benzyl-2-butyl-2-methylcyclopropane-1-carboxylate (2a$_{anti}$):



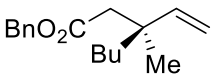
R_f = 0.61 (Hexane/Et_2O = 98:2); Yield: 75% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): 0.74-0.79 (m, 4H), 1.09 (s, 3H), 1.10-1.19 (m, 4H), 1.24-1.31 (m, 1H), 1.36-1.48 (m, 3H), 5.03 (s, 2H), 7.22-7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.2, 22.8, 24.1, 26.7, 27.6, 29.3, 31.9, 66.2, 128.1, 128.3, 128.5, 136.3, 172.7; HRMS (ESI) calcd. for $C_{16}H_{23}O_2$ $[M+H]^+$: 247.1698; found: 247.1701.
Note: The stereochemistry was determined through the NOESY experiment (spectrum available below).

Benzyl-2-butyl-2-methylcyclopropane-1-carboxylate (2a$_{syn}$):



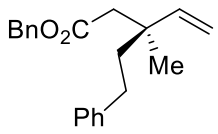
R_f = 0.61 (Hexane/Et_2O = 98:2); Yield: 72% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): 0.77-0.83 (m, 4H), 1.01 (t, *J* = 5.2 Hz, 1H), 1.1 (s, 3H), 1.18-1.29 (m, 6H), 1.47 (q, *J* = 2.4 Hz, 1H), 5.01 (d, *J* = 12.4 Hz, 1H), 5.07 (d, *J* = 12.4 Hz, 1H), 7.24-7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 16.2, 21.5, 22.7, 26.3, 27.2, 28.8, 40.5, 66.1, 128.0, 128.1, 128.5, 136.5, 172.7; HRMS (ESI) calcd. for $C_{16}H_{23}O_2$ $[M+H]^+$: 247.1698; found: 247.1700.
*Note: The stereochemistry was determined comparing the NOESY and ^{13}C experiments with the **2a$_{anti}$** (spectrum available below). In **2a$_{syn}$**, due to the shielding effect of the ester group, carbon syn to it resulting in an upfield signal.*

Benzyl 3-butyl-3-methylpent-4-enoate (4a):



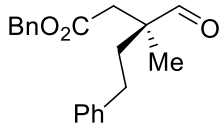
R_f = 0.59 (Hexane/Et_2O = 98:2); Yield: 72% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.2 Hz, 3H), 1.09 (s, 3H), 1.16-1.23 (m, 4H), 1.34-1.38 (m, 2H), 2.34 (s, 2H), 4.91 (dd, *J* = 0.8, 18.0 Hz, 1H), 4.98 (dd, *J* = 0.8, 10.8 Hz, 1H), 5.06 (s, 2H), 5.78 (dd, *J* = 10.8, 18.0 Hz, 1H), 7.29-7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 23.2, 23.3, 26.3, 39.3, 40.5, 45.0, 65.9, 111.9, 128.1, 128.3, 128.5, 136.1, 145.7, 171.7; HRMS (ESI) calcd. for $C_{17}H_{25}O_2$ $[M+H]^+$: 261.1855; found: 261.1855.

(*S*)-Benzyl 3-methyl-3-phenethylpent-4-enoate ((*S*)-4b):



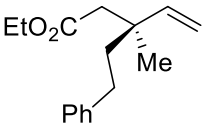
R_f = 0.47 (Hexane/Et_2O = 98:2); Yield: 70% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (s, 3H), 1.61-1.66 (m, 2H), 2.37 (s, 2H), 2.45 (dd, *J* = 6.4, 10.8 Hz, 2H), 4.93 (d, *J* = 17.6 Hz, 1H), 5.00 (d, *J* = 10.8 Hz, 1H), 5.02 (s, 2H), 5.80 (dd, *J* = 10.8, 17.6 Hz, 1H), 7.02-7.10 (m, 3H), 7.15-7.19 (m, 2H), 7.25-7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5, 30.7, 39.4, 42.6, 44.8, 66.1, 112.6, 125.6, 128.2, 128.3 (x2), 128.4, 128.5, 135.9, 142.6, 145.2, 171.5; HRMS (ESI) calcd. for $C_{21}H_{24}O_2Na$ $[M+Na]^+$: 331.1674; found: 331.1658; $[\alpha]_D$: ($CHCl_3$, c = 0.22): 0.53°.
*Note: The determination of the enantiomeric excess couldn't be done on the **(S)-4b** by HPLC with CHIRALPAK® AD-H, AY-H, IA or CHIRALCEL® OD columns, but after ozonolysis on the aldehyde **(S)-5b**.*

(*S*)-Benzyl 3-formyl-3-methyl-5-phenylpentanoate ((*S*)-5b):



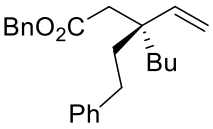
R_f = 0.36 (Hexane/Et_2O = 90:10); Yield: 62% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 3H), 1.68-1.82 (m, 2H), 2.38-2.50 (m, 2H), 2.52 (d, *J* = 15.6 Hz, 1H), 2.63 (d, *J* = 15.6 Hz, 1H), 5.03 (s, 2H), 7.00-7.01 (m, 2H), 7.08-7.11 (m, 1H), 7.15-7.19 (m, 2H), 7.22-7.29 (m, 5H), 9.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4, 30.5, 37.7, 40.2, 47.9, 66.8, 126.3, 128.4, 128.6, 128.6, 128.7, 128.8, 135.7, 141.5, 171.0, 204.1; HRMS (ESI) calcd. for $C_{20}H_{23}O_3$ $[M+H]^+$: 311.1647; found: 311.1650; e.r. = 96:4. The chiral sample was analyzed by HPLC using a CHIRALPAK® AY-H column (10mmØ×20mmL), n-hexane/isopropanol 90:10, 1 mL/min, 210nm. t_R (major) = 9.78 min, t_R (minor) = 8.12 min.

Ethyl 3-methyl-3-phenethylpent-4-enoate (4c):



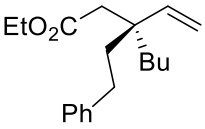
R_f = 0.52 (Hexane/Et_2O = 98:2); Yield: 71% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (s, 3H), 1. 17 (t, *J* = 7.2 Hz, 3H), 1.63-1.68 (m, 2H), 2.31 (dd, *J* = 13.6, 14.4 Hz, 2H), 2.46-2.50 (m, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.94 (dd, *J* = 0.8, 17.6 Hz, 1H), 5.02 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.80 (dd, *J* = 10.8, 17.6 Hz, 1H), 7.08-7.10 (m, 3H), 7.18-7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 23.4, 30.7, 39.3, 42.6, 44.8, 60.09, 112.4, 125.6, 128.3 (x2), 142.7, 145.3, 171.6; HRMS (ESI) calcd. for $C_{16}H_{23}O_2$ $[M+H]^+$: 247.1698; found: 247.1634.

Benzyl 3-butyl-3-phenethylpent-4-enoate (4d):



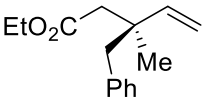
R_f = 0.54 (Hexane/Et_2O = 98:2); Yield: 64% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.8 Hz, 3H), 1.17-1.28 (bs, 6H), 1.40-1.47 (m, 1H), 1.63-1.77 (m, 2H), 2.46-2.53 (m, 3H), 4.90 (d, *J* = 17.6 Hz, 1H), 5.07-5.10 (m, 3H), 5.72 (dd, *J* = 11.2, 17.6 Hz, 1H), 7.05-7.14 (m, 3H), 7.18-7.22 (m, 2H), 7.26-7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 23.2, 25.8, 30.3, 37.2, 39.5, 40.3, 42.3, 66.1, 113.2, 125.6, 128.2, 128.3, 128.4, 128.5, 128.6, 136.0, 142.8, 144.9, 171.6; HRMS (ESI) calcd. for $C_{24}H_{31}O_2$ $[M+H]^+$: 351.2280; found: 351.2319.

Ethyl 3-butyl-3-phenethylpent-4-enoate (4e):



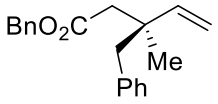
R_f = 0.57 (Hexane/Et_2O = 98:2); Yield: 68% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.8 Hz, 3H), 1.16-1.20 (m, 7H), 1.34-1.45 (m, 2H), 1.57-1.75 (m, 2H), 2.36 (s, 2H), 2.41-2.56 (m, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 4.88 (d, *J* = 17.6 Hz, 1H), 5.05 (d, *J* = 11.2 Hz, 1H), 5.69 (dd, *J* = 11.2, 17.6 Hz, 1H), 7.08-7.11 (m, 3H), 7.18-7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.3, 23.3, 25.8, 30.2, 37.1, 39.5, 40.4, 42.2, 60.0, 113.0, 125.6, 128.3, 128.3, 142.9, 145.0, 171.8; HRMS (ESI) calcd. for $C_{19}H_{29}O_2$ $[M+H]^+$: 289.2156; found: 289.2168.

Ethyl 3-methyl-3-benzylpent-4-enoate (4f):



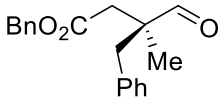
R_f = 0.52 (Hexane/Et_2O = 98:2); Yield: 75% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 3H), 1. 17 (t, *J* = 7.2 Hz, 3H), 2.19 (d, *J* = 14 Hz, 1H), 2.27 (d, *J* = 14 Hz, 1H), 2.65 (d, *J* = 13.6 Hz, 1H), 2.70 (d, *J* = 14.8 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.82 (dd, *J* = 0.8, 17.6 Hz, 1H), 4.94 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.83 (dd, *J* = 10.8, 17.6 Hz, 1H), 7.07-7.09 (m, 2H), 7.13-7.20 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 23.3, 40.0, 44.1, 46.8, 60.0, 112.3, 126.2, 127.7, 130.8, 137.8, 145.2, 171.8; HRMS (ESI) calcd. for $C_{15}H_{21}O_2$ $[M+H]^+$: 233.1542; found: 233.1519.

(*S*)-Benzyl 3-methyl-3-benzylpent-4-enoate ((*S*)-4g):



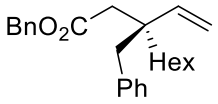
R_f = 0.49 (Hexane/Et_2O = 98:2); Yield: 72% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, 3H), 2.25 (d, *J* = 14.0 Hz, 1H), 2.32 (d, *J* = 14.0 Hz, 1H), 2.65 (d, *J* = 13.2 Hz, 1H), 2.69 (d, *J* = 13.6 Hz, 1H), 4.80 (d, *J* = 17.6 Hz, 1H), 4.92 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.02 (s, 2H), 5.82 (dd, *J* = 10.8, 17.6 Hz, 1H), 7.03-7.05 (m, 2H), 7.12-7.18 (m, 3H), 7.24-7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.4, 40.1, 44.0, 46.8, 66.1, 112.5, 126.2, 127.7, 128.2, 128.4, 128.5, 130.8, 136.0, 137.7, 145.1, 171.6; HRMS (ESI) calcd. for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1657; found: 295.1693; $[\alpha]_D$: ($CHCl_3$, c = 0.14): 14.76°.
Note: The determination of the enantiomeric excess couldn't be done on the ***(S)-4g*** *by HPLC with CHIRALPAK® AD-H, AY-H, IA or CHIRALCEL® OD columns, but after ozonolysis on the aldehyde* ***(S)-5g****.*

(*S*)-Benzyl 3-benzyl-3-methyl-4-oxobutanoate ((*S*)-5g):



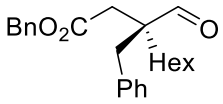
R_f = 0.37 (Hexane/Et_2O = 90:10); Yield: 69% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (s, 3H), 2.38 (d, *J* = 15.6 Hz, 1H), 2.56 (d, *J* = 16.4 Hz, 1H), 2.76 (d, *J* = 13.6 Hz, 1H), 2.81 (d, *J* = 13.6 Hz, 1H), 5.01 (d, *J* = 12.4 Hz, 1H), 5.04 (d, *J* = 12.4 Hz, 1H), 6.96-6.98 (m, 2H), 7.12-7.19 (m, 3H), 7.23-7.50 (m, 5H), 9.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.7, 39.8, 41.7, 48.6, 66.8, 127.0, 128.5, 128.6, 128.7, 128.8, 130.6, 1357, 135.9, 171.1, 204.5; HRMS (ESI) calcd. for $C_{19}H_{21}O_3$ $[M+H]^+$: 297.1491; found: 297.1496; e.r. = 93:7. The chiral sample was analyzed by HPLC using a CHIRALPAK® AD-H column (4.6mmØ×250mmL), n-hexane/isopropanol 90:10, 1 mL/min, 210 nm. t_R (major) = 7.85 min, t_R (minor) = 7.36 min.

(*S*)-Benzyl 3-hexyl-3-benzylpent-4-enoate ((*S*)-4h):



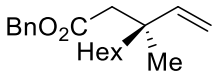
R_f = 0.56 (Hexane/Et_2O = 98:2); Yield: 73% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.22-1.27 (m, 8H), 1.32-1.39 (m, 1H), 1.46-1.52 (m, 1H), 2.30 (d, *J* = 14.8 Hz, 1H), 2.39 (d, *J* = 14.8 Hz, 1H), 2.76 (d, *J* = 13.2 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 4.76 (d, *J* = 18.0 Hz, 1H), 5.03 (d, *J* = 11.2 Hz, 1H), 5.12 (s, 2H), 5.74 (dd, *J* = 11.2, 18.0 Hz, 1H), 7.13-7.25 (m, 5H), 7.32-7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 23.9, 29.8, 31.8, 37.2, 39.1, 43.2, 43.6, 66.0, 113.0, 126.1, 127.7, 128.2, 128.4, 128.5, 130.9, 136.0, 137.8, 144.6, 171.9; HRMS (ESI) calcd. for $C_{25}H_{33}O_2$ $[M+H]^+$: 365.2427; found: 365.2475; $[\alpha]_D$: ($CHCl_3$, c = 0.24): 0.46°.
Note: The determination of the enantiomeric excess couldn't be done on the ***(S)-4h*** *by HPLC with CHIRALPAK® AD-H, AY-H, IA or CHIRALCEL® OD columns, but after ozonolysis on the aldehyde* ***(S)-5h****.*

(*S*)-Benzyl 3-benzyl-3-hexyl-4-oxobutanoate ((*S*)-5h):



R_f = 0.41 (Hexane/Et_2O = 90:10); Yield: 72% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.2 Hz, 3H), 1.20-1.24 (m, 8H), 1.57 (bs, 2H), 2.46 (d, *J* = 16.4 Hz, 1H), 2.52 (d, *J* = 16.4 Hz, 1H), 2.97 (s, 2H), 5.08 (d, *J* = 12.0 Hz, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 7.00-7.03 (m, 2H), 7.18-7.24 (m, 3H), 7.30-7.35 (m, 5H), 9.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 22.7, 23.9, 29.9, 31.7, 33.5, 36.3, 39.2, 52.4, 66.4, 126.9, 128.5, 128.6, 128.7. 128.8, 130.5, 135.9, 136.3, 171.4, 204.8; HRMS (ESI) calcd. for $C_{24}H_{31}O_3$ $[M+H]^+$: 367.2273; found: 367.2279; e.r. = 93:7. The chiral sample was analyzed by HPLC using a CHIRALCEL® OD column (4.6mmØ×250mmL), n-hexane/isopropanol 99:1, 1 mL/min, 210 nm. t_R (major) = 9.62 min, t_R (minor) = 10.42 min.

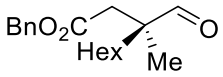
(*S*)-Benzyl 3-hexyl-3-methylpent-4-enoate ((*S*)-4i):



R_f = 0.63 (Hexane/Et_2O = 98:2); Yield: 65% (Colorless oil)
^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.8 Hz, 3H), 1.09 (s, 3H), 1.19-1.25 (m, 8H), 1.33-1.37 (m, 2H), 2.34 (s, 2H), 4.90 (dd, *J* = 0.8, 17.5 Hz, 1H), 4.96 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.06 (s, 2H), 5.78 (dd, *J* = 10.8, 17.5 Hz, 1H), 7.28-7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.9, 23.5, 24.2, 30.1, 32.0, 39.5, 40.9, 45.2, 66.2, 112.1, 128.3, 128.5, 128.7, 136.3, 145.9, 171.9; HRMS (ESI) calcd. for $C_{19}H_{29}O_2$ $[M+H]^+$: 289.2156; found: 289.2168; $[\alpha]_D$: ($CHCl_3$, c = 0.32): 20.81°.

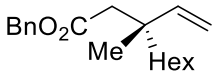
Note: The determination of the enantiomeric excess couldn't be done on the ***(S)-4i*** *by HPLC with CHIRALPAK® AD-H, AY-H, IA or CHIRALCEL® OD columns, but after ozonolysis on the aldehyde* ***(S)-5i****.*

(*S*)-Benzyl 3-formyl-3-methylnonanoate ((*S*)-5i):



R_f = 0.52 (Hexane/Et_2O = 90:10); Yield: 70% (Colorless oil)
^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3H), 1.14 (s, 3H), 1.16-1.29 (m, 8H), 1.42-1.58 (m, 2H), 2.51 (d, *J* = 15.6 Hz, 1H), 2.65 (d, *J* = 15.6 Hz, 1H), 5.09 (s, 2H), 7.31-7.35 (m, 5H), 9.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 19.0, 22.5, 23.7, 29.7, 31.6, 35.7, 40.1, 47.7, 66.5, 128.3, 128.4, 128.6, 135.6, 171.0, 204.5; HRMS (ESI) calcd. for $C_{18}H_{27}O_3$ $[M+H]^+$: 291.1882; found: 291.1955; e.r. = 91:9. The chiral sample was analyzed by HPLC using a CHIRALCEL® OD column (4.6mmØ×250mmL), n-hexane/isopropanol 90:10, 1 mL/min, 210 nm. t_R (major) = 5.87 min, t_R (minor) = 5.19 min.

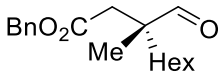
(*R*)-Benzyl 3-hexyl-3-methylpent-4-enoate ((*R*)-4i):



R_f = 0.63 (Hexane/Et_2O = 98:2); Yield: 63% (Colorless oil)
Spectral data of the title compound were identical to the (*S*)-Benzyl 3-formyl-3-methylnonanoate.

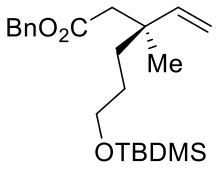
Note: The determination of the enantiomeric excess couldn't be done on the ***(R)-4i*** *by HPLC with CHIRALPAK® AD-H, AY-H, IA or CHIRALCEL® OD columns, but after ozonolysis on the aldehyde* ***(R)-5i****.*

(*R*)-Benzyl 3-formyl-3-methylnonanoate ((*R*)-5i):



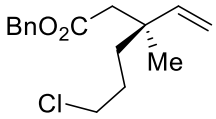
R_f = 0.52 (Hexane/Et_2O = 90:10); Yield: 72% (Colorless oil)
Spectral data of the title compound were identical to the (*S*)-Benzyl 3-formyl-3-methylnonanoate. e.r. = 90:10. The chiral sample was analyzed by HPLC using a CHIRALCEL® OD column (4.6mmØ×250mmL), n-hexane/isopropanol 90:10, 1 mL/min, 210 nm. t_R (major) = 5.24 min, t_R (minor) = 5.91 min.

Benzyl 6-((*tert*-butyldimethylsilyl)oxy)-3-methyl-3-vinylhexanoate (4j):



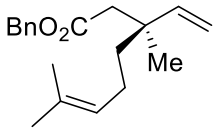
R_f = 0.62 (Hexane/Et_2O = 98:2); Yield: 70% (Colorless oil)
^1H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 6H), 0.88 (s, 9H), 1.11 (s, 3H), 1.42-1.45 (m, 4H), 2.37 (s, 2H), 3.53 (t, *J* = 5.6 Hz, 2H), 4.93 (dd, *J* = 0.8, 17.6 Hz, 1H), 4.99 (dd, *J* = 0.8, 10.8 Hz, 1H), 5.07 (s, 2H), 5.79 (dd, *J* = 10.8, 18.0 Hz, 1H), 7.32-7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = -5.2 (x2), 18.4, 23.2, 25.9 (x3), 27.6, 36.6, 39.0, 45.2, 63.6, 66.0, 112.3, 128.2, 128.3, 128.5, 136.1, 145.4, 171.6; HRMS (ESI) calcd. for $C_{22}H_{37}O_3Si$ $[M+H]^+$: 377.2531; found: 377.2506.

Benzyl 6-chloro-3-methyl-3-vinylhexanoate (4k):



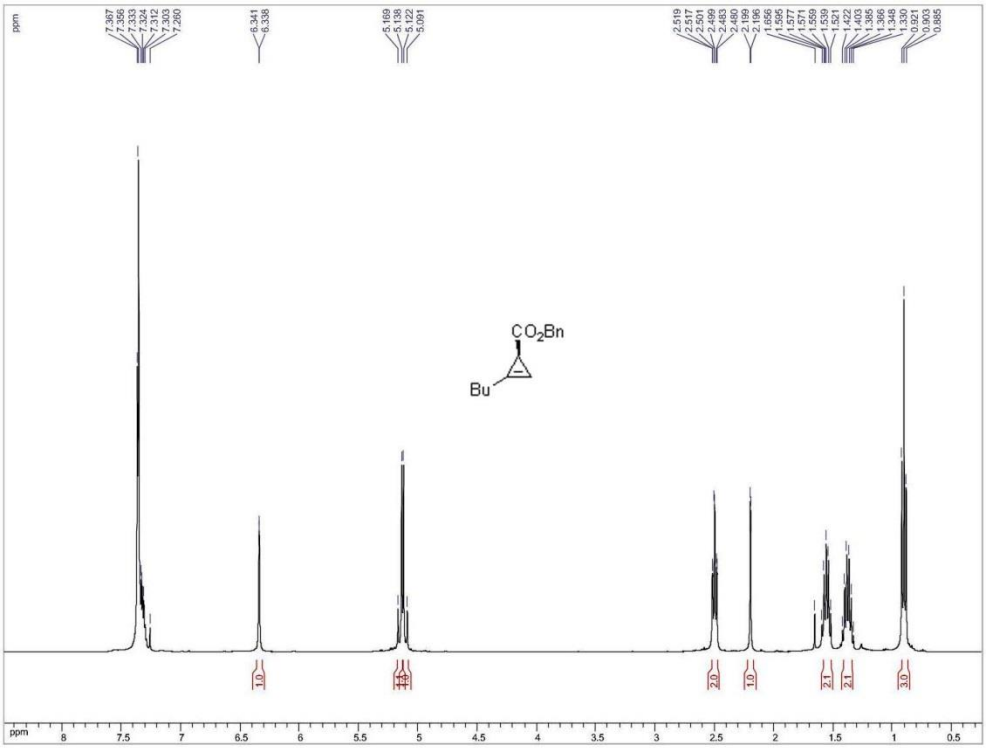
R_f = 0.46 (Hexane/Et_2O = 98:2); Yield: 71% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 3H), 1.48-1.53 (m, 2H), 1.65-1.71 (m, 2H), 2.36 (s, 2H), 3.43 (t, *J* = 6.4 Hz, 2H), 4.94 (dd, *J* = 0.8, 17.2 Hz, 1H), 5.02 (dd, *J* = 0.8, 10.8 Hz, 1H), 5.07 (s, 2H), 5.76 (dd, *J* = 10.8, 17.2 Hz, 1H), 7.31-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.4, 27.6, 37.6, 38.9, 44.9, 45.4, 66.1, 112.7, 128.2, 128.4, 128.5, 135.9, 144.9, 171.3; HRMS (ESI) calcd. for $C_{16}H_{22}ClO_2$ $[M+H]^+$: 281.1308; found: 281.1313

Benzyl 3,7-dimethyl-3-vinyloct-6-enoate (4l):

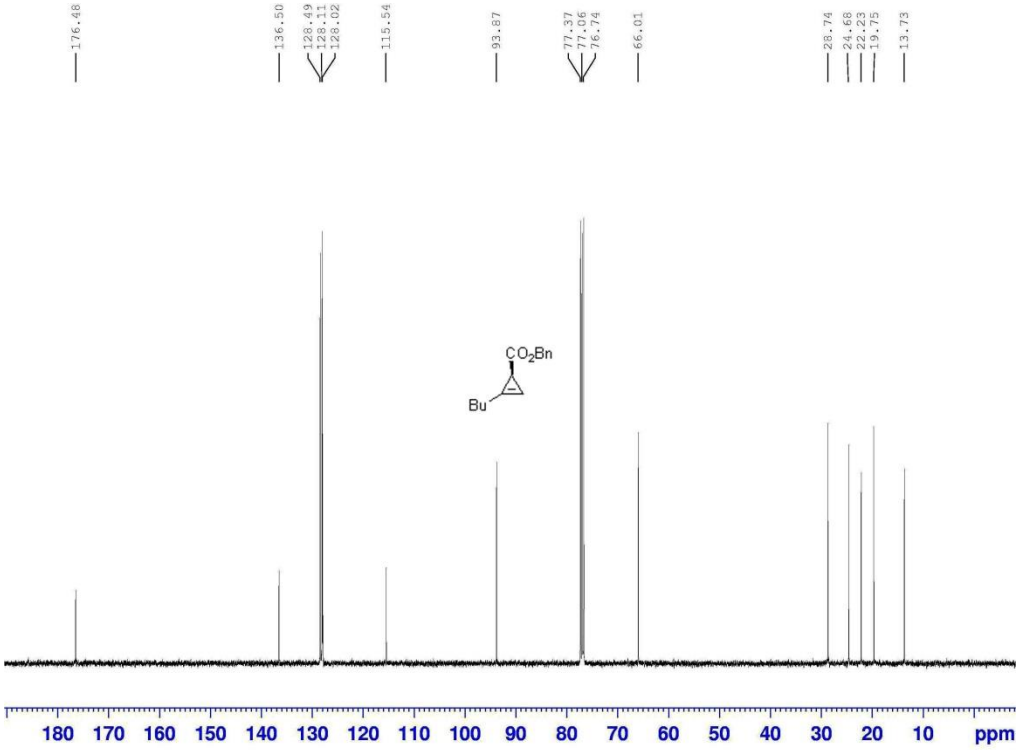


R_f = 0.49 (Hexane/Et_2O = 98:2); Yield: 64% (Colorless oil)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (s, 3H), 1.38-1.43 (m, 2H), 1.56 (s, 3H), 1.66 (s, 3H), 1.88-1.91 (m, 2H), 2.37 (s, 2H), 4.93 (dd, *J* = 0.8, 17.6 Hz, 1H), 4.99-5.04 (m, 2H), 5.08 (s, 2H), 5.81 (dd, *J* = 10.8, 17.6 Hz, 1H), 7.33-7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5, 22.8, 23.2, 25.6, 39.3, 40.6, 44.9, 66.0, 112.2, 124.4, 128.1, 128.3, 128.5, 131.4, 136.0, 145.4, 171.6; HRMS (ESI) calcd. for $C_{19}H_{27}O_2$ $[M+H]^+$: 287.2019; found: 287.2006.

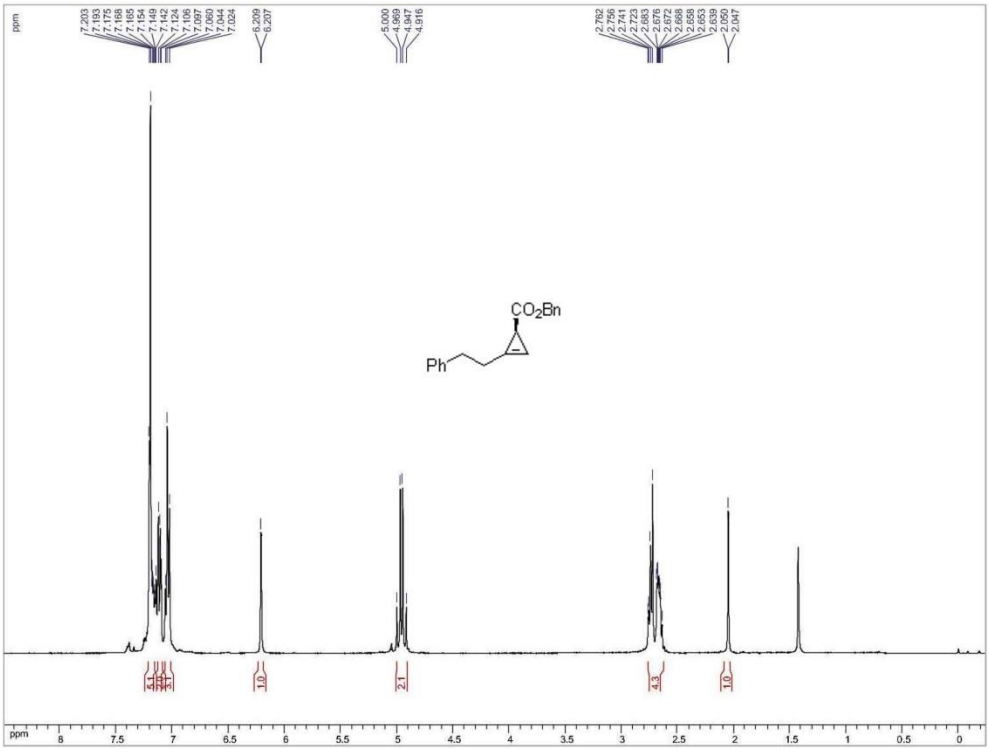
^{1}H NMR spectrum of 1a (400 MHz, $CDCl_3$):



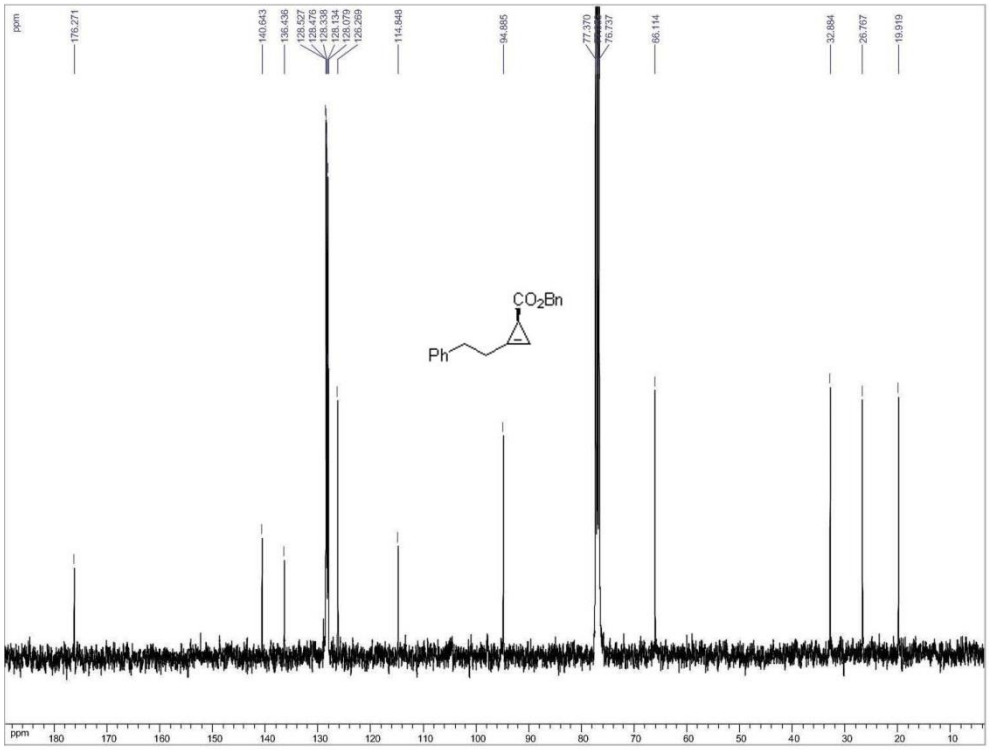
^{13}C NMR spectrum of 1a (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of 1b (400 MHz, $CDCl_3$):

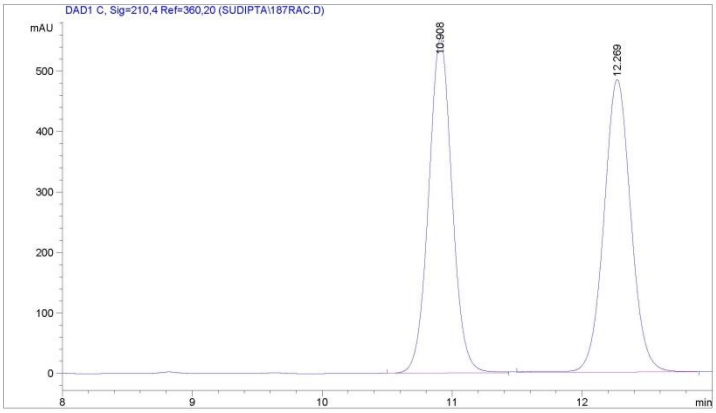


^{13}C NMR spectrum of 1b (100 MHz, $CDCl_3$):



HPLC analysis of the racemic and enantioenriched 1b:

IA
Hex/iPrOH = 99:1
1 mL/min

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                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|------|----------|----------|--------|
   1  10.908 BB    0.1942 6929.55859  553.08447  49.7835
   2  12.269 BB    0.2225 6989.81592  484.00760  50.2165

Totals :                  1.39194e4  1037.09207

 Results obtained with enhanced integrator!
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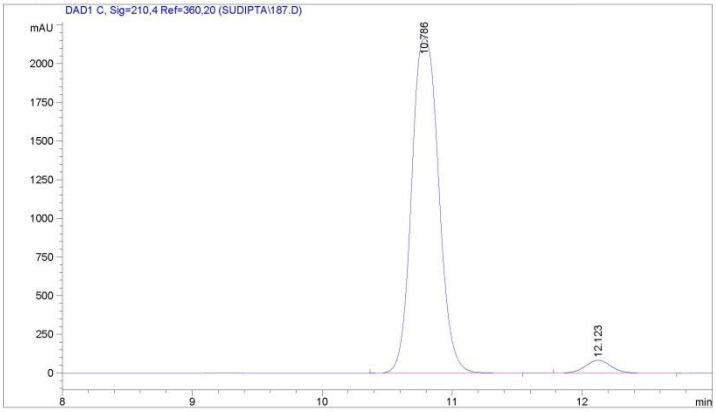
IA
Hex/iPrOH = 99:1
1 mL/min

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|------|----------|----------|--------|
   1  10.786 BB    0.2289 3.13138e4  2163.45410  96.3537
   2  12.123 BB    0.2164 1185.01807   84.07507   3.6463

Totals :                  3.24988e4  2247.52917

 Results obtained with enhanced integrator!
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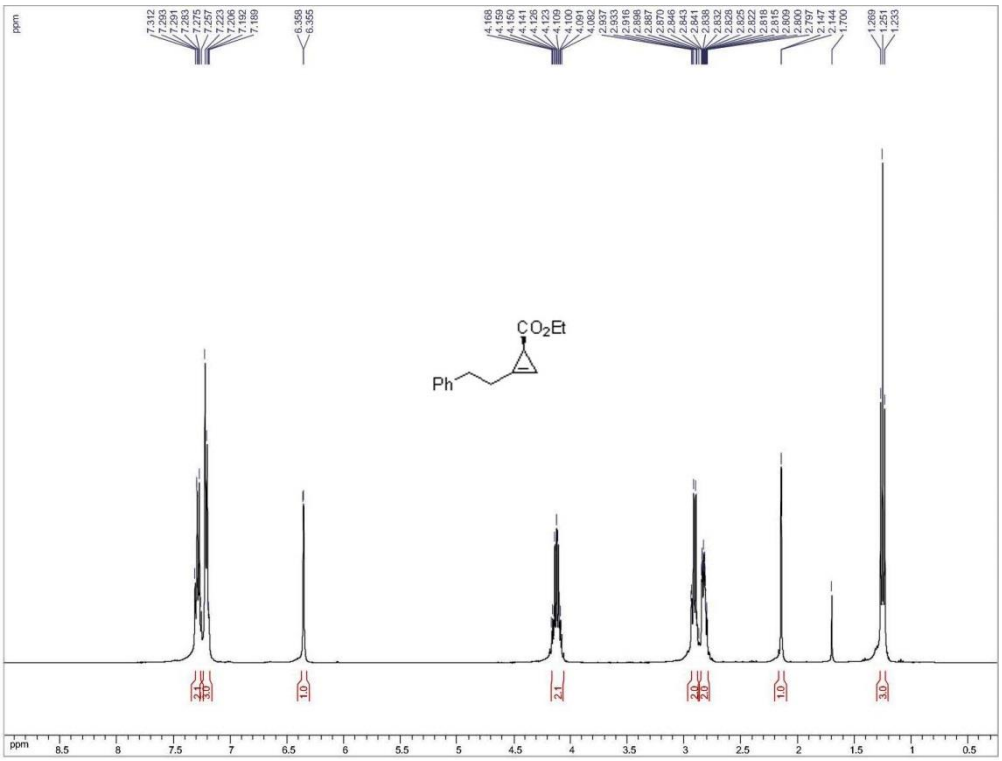
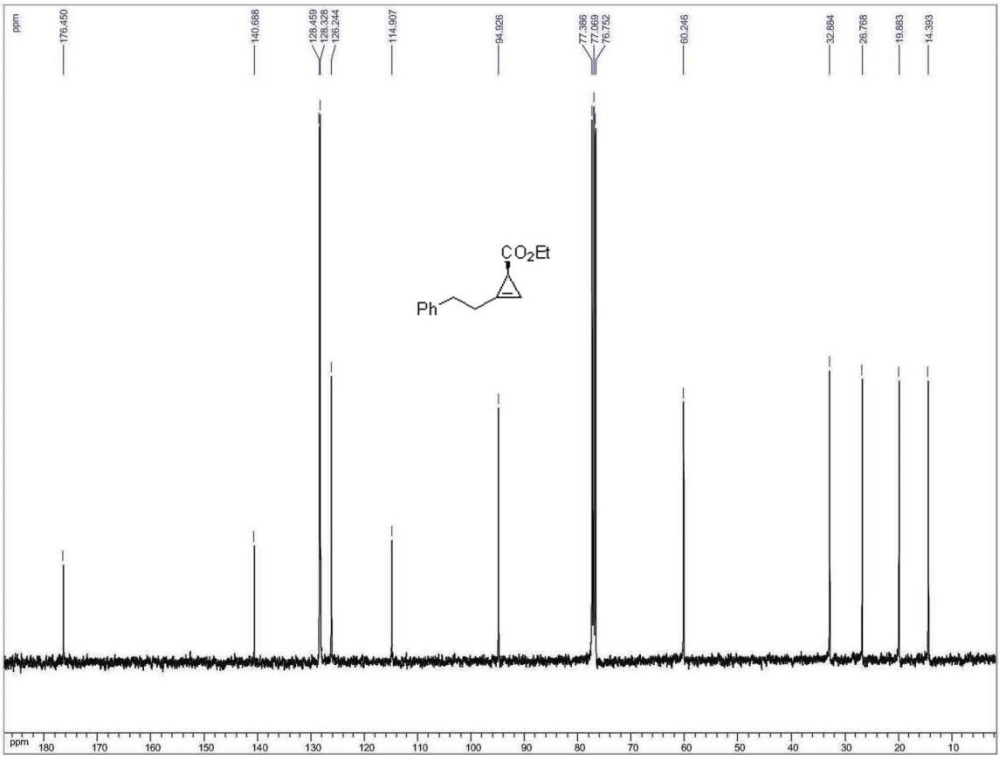
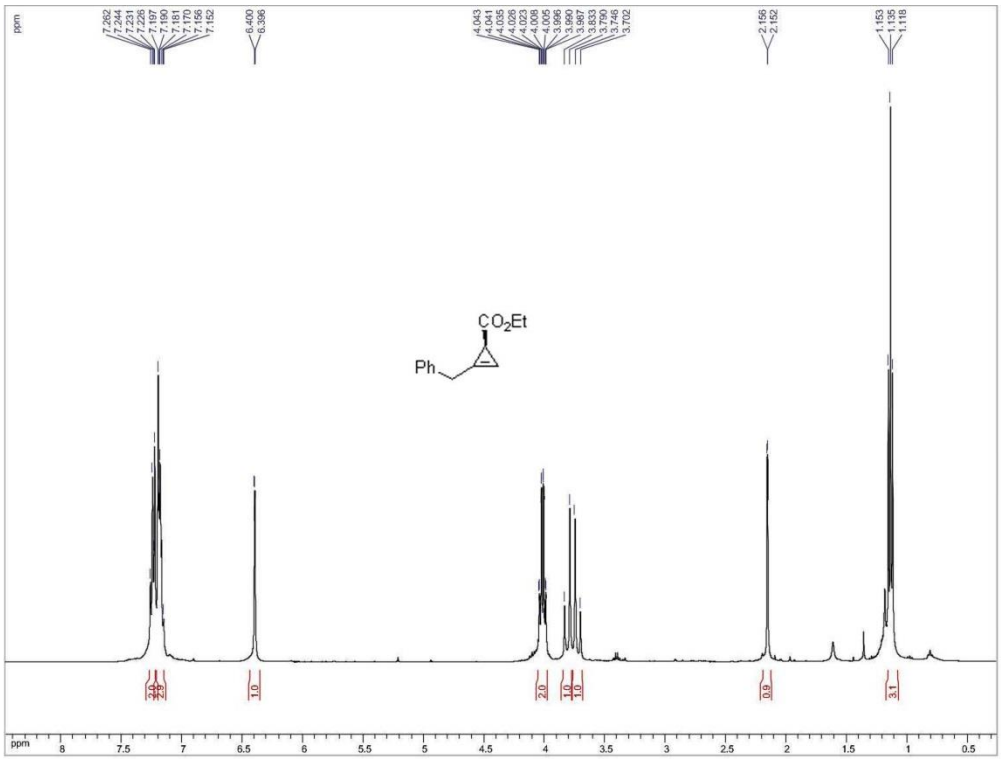
^{1}H NMR spectrum of 1c (400 MHz, $CDCl_3$):



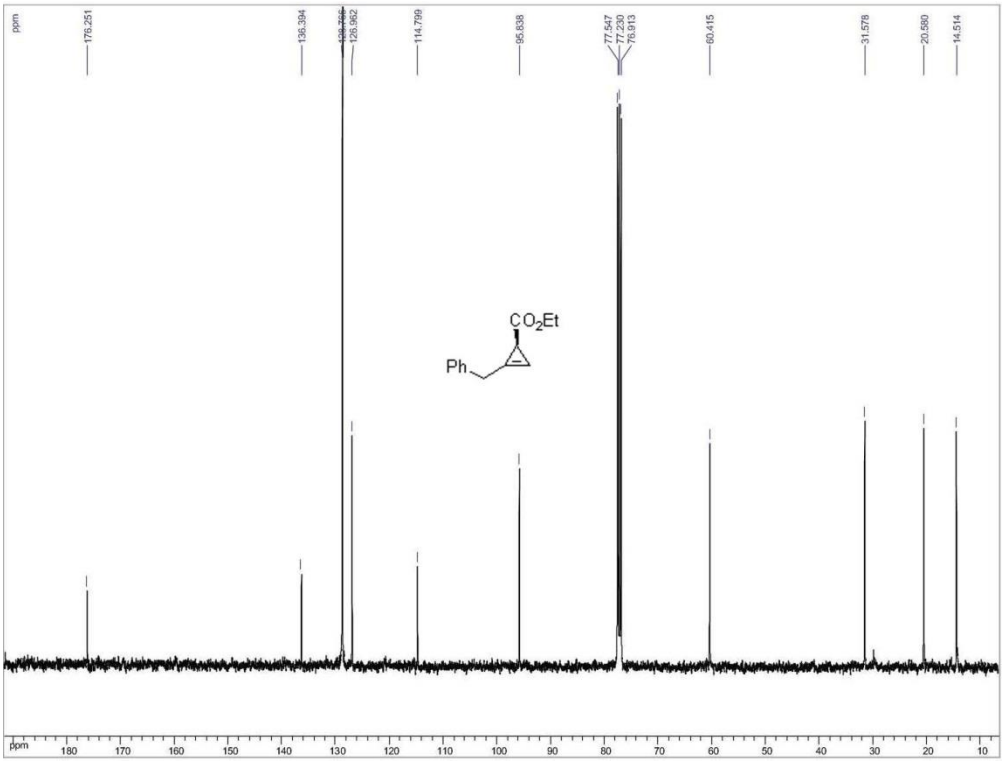
^{13}C NMR spectrum of 1c (100 MHz, $CDCl_3$):



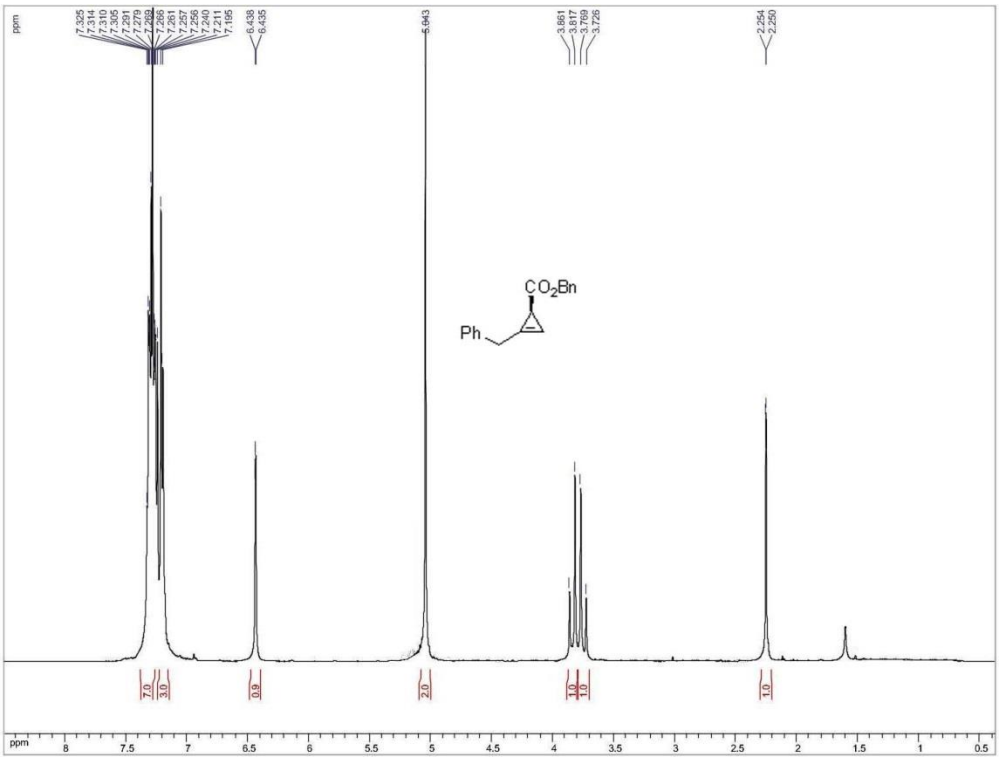
^{1}H NMR spectrum of 1d (400 MHz, $CDCl_3$):



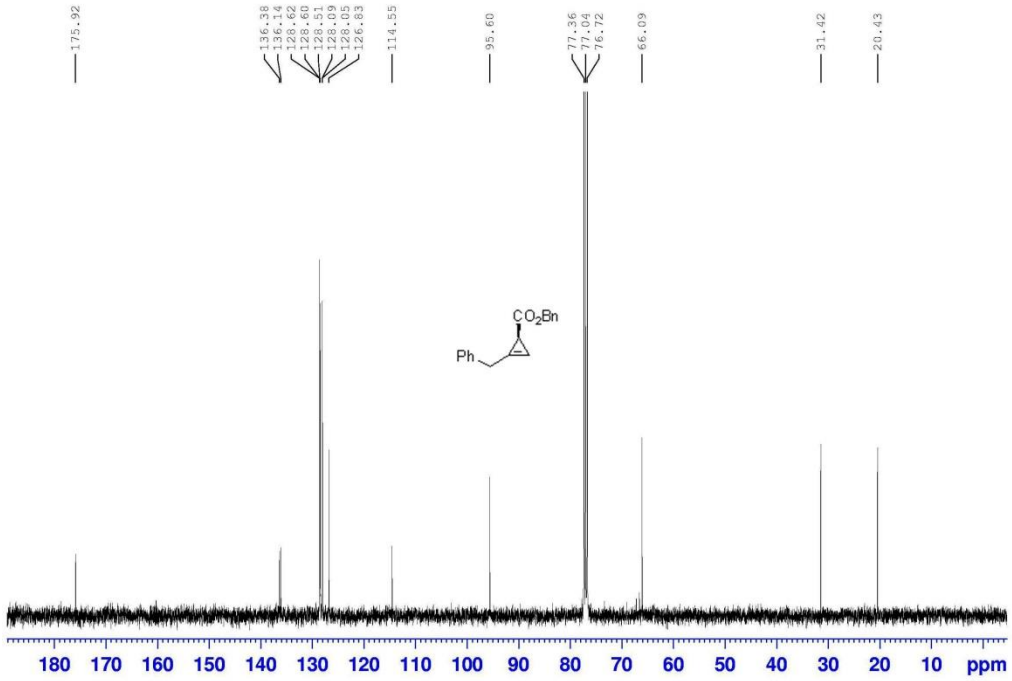
^{13}C NMR spectrum of 1d (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of 1e (400 MHz, $CDCl_3$):

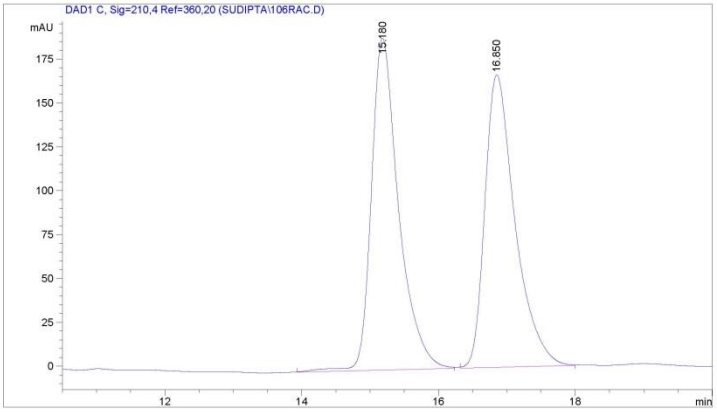


^{13}C NMR spectrum of 1e (100 MHz, $CDCl_3$):



HPLC analysis of the racemic and enantioenriched 1e:

Chiral OD
Hex:iPrOH = 99:1
1 ml/min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

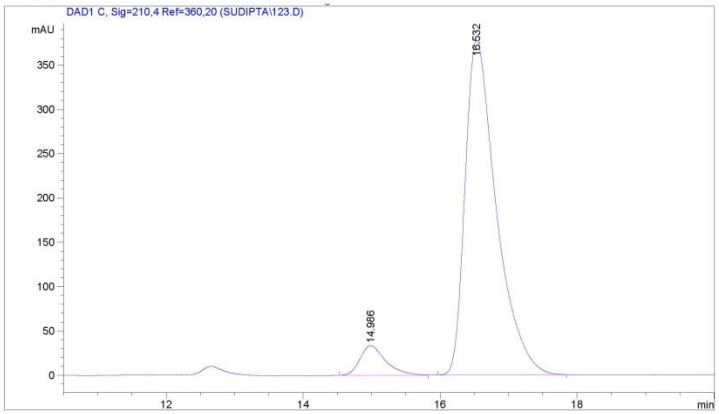
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.180	BB	0.4158	5249.95117	189.13080	50.7000
2	16.850	BB	0.4595	5104.97656	166.59854	49.3000

Totals : 1.03549e4 355.72934

Results obtained with enhanced integrator!

*** End of Report ***

Chiral OD
Hex:iPrOH = 99:1
1 ml/min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

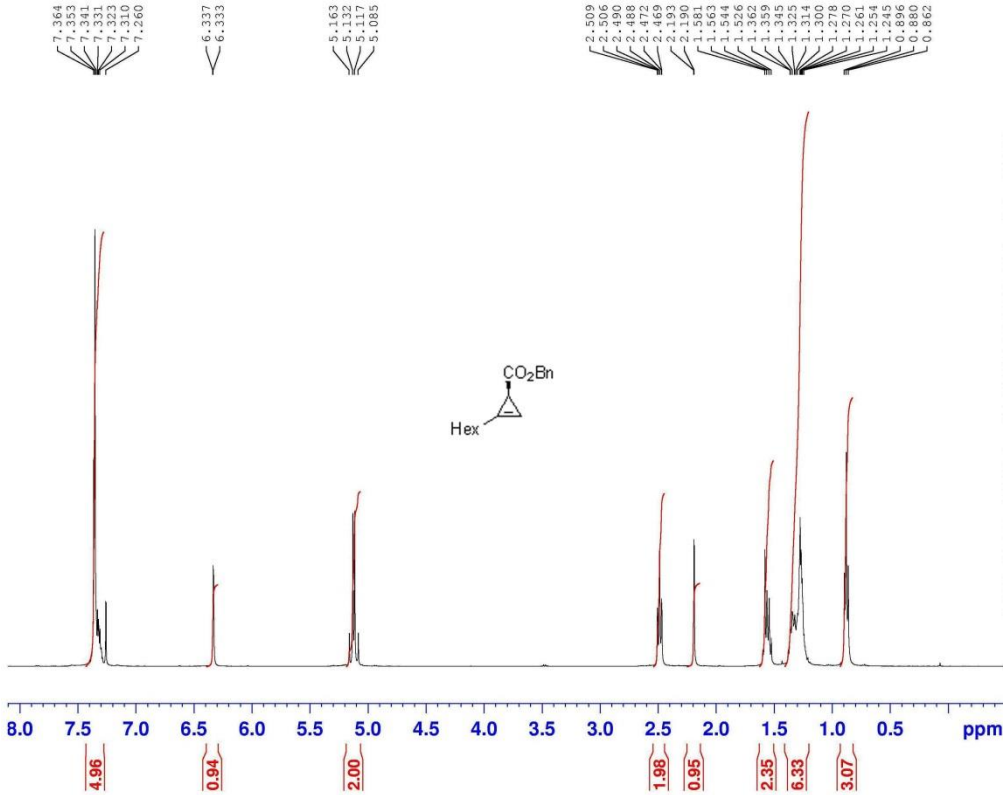
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.986	BB	0.3937	885.28436	33.56318	6.8841
2	16.532	BB	0.4819	1.19746e4	377.63043	93.1159

Totals : 1.28598e4 411.19361

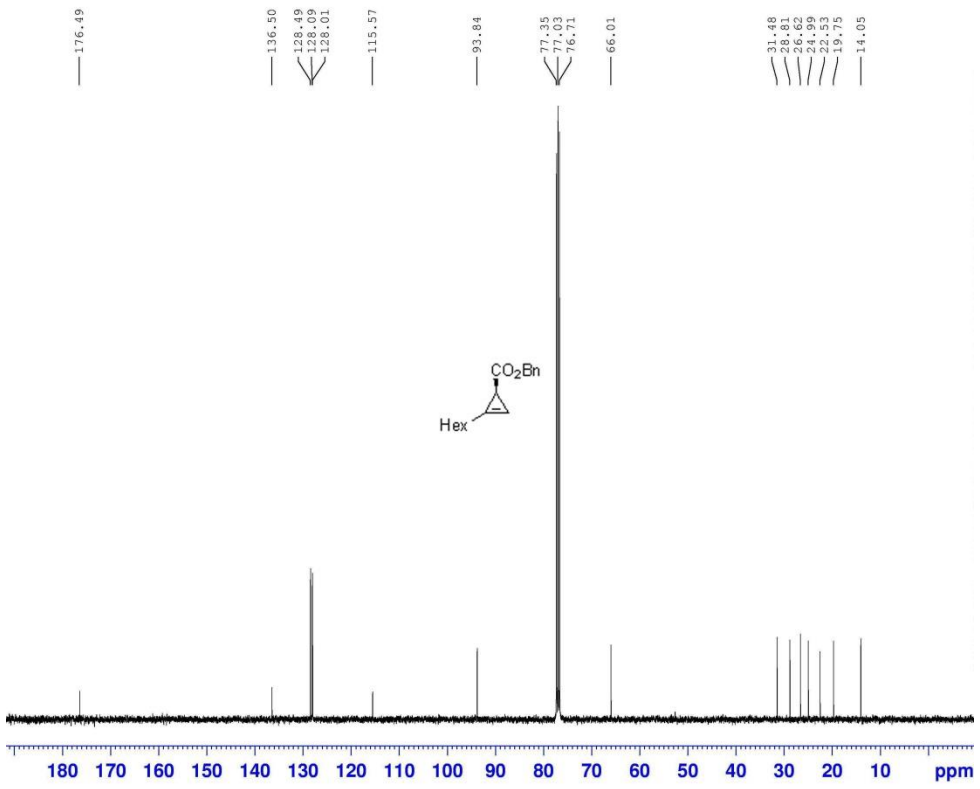
Results obtained with enhanced integrator!

*** End of Report ***

^{1}H NMR spectrum of 1f (400 MHz, $CDCl_3$):

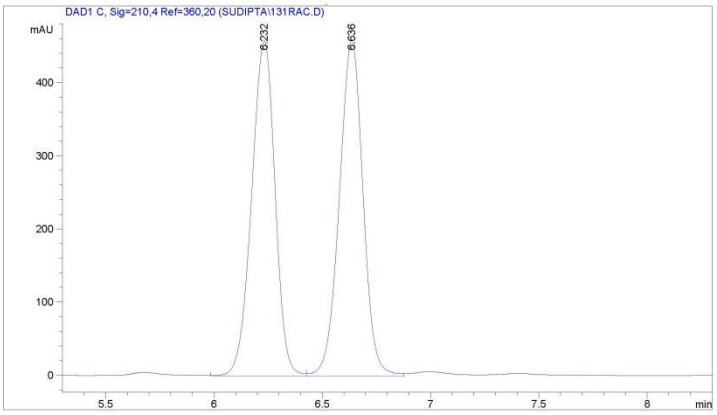


^{13}C NMR spectrum of 1f (100 MHz, $CDCl_3$):



HPLC analysis of the racemic and enantioenriched 1f:

IA
Hex:iPrOH = 99:1
1 mL/min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

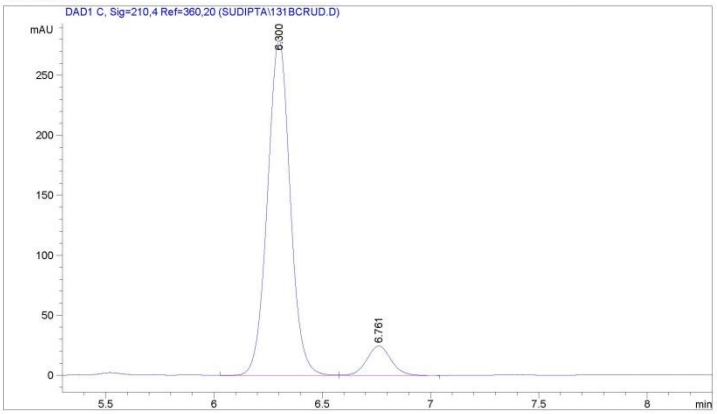
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.232	VV	0.1176	3446.57910	458.94766	49.7436
2	6.636	VV	0.1165	3482.11475	459.05258	50.2564

Totals : 6928.69385 918.00024

Results obtained with enhanced integrator!

*** End of Report ***

IA
Hex:iPrOH = 99:1
1.0 ml/min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

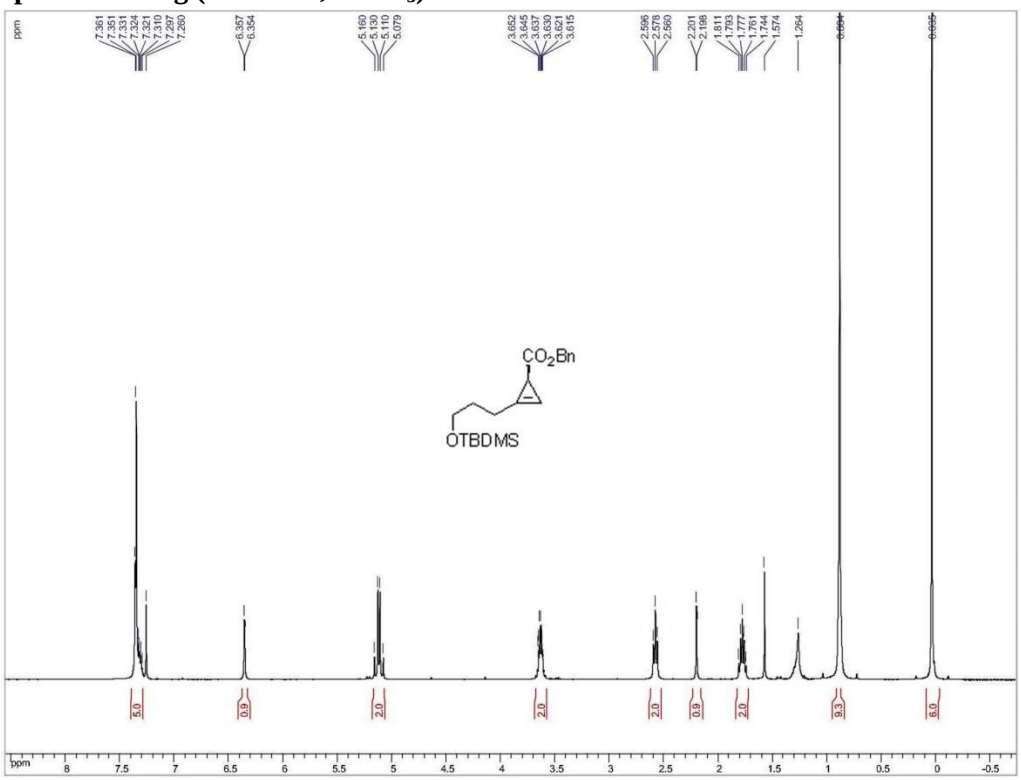
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.300	VV	0.1131	2042.13733	279.89413	91.3658
2	6.761	VP	0.1191	192.98381	24.71037	8.6342

Totals : 2235.12114 304.60450

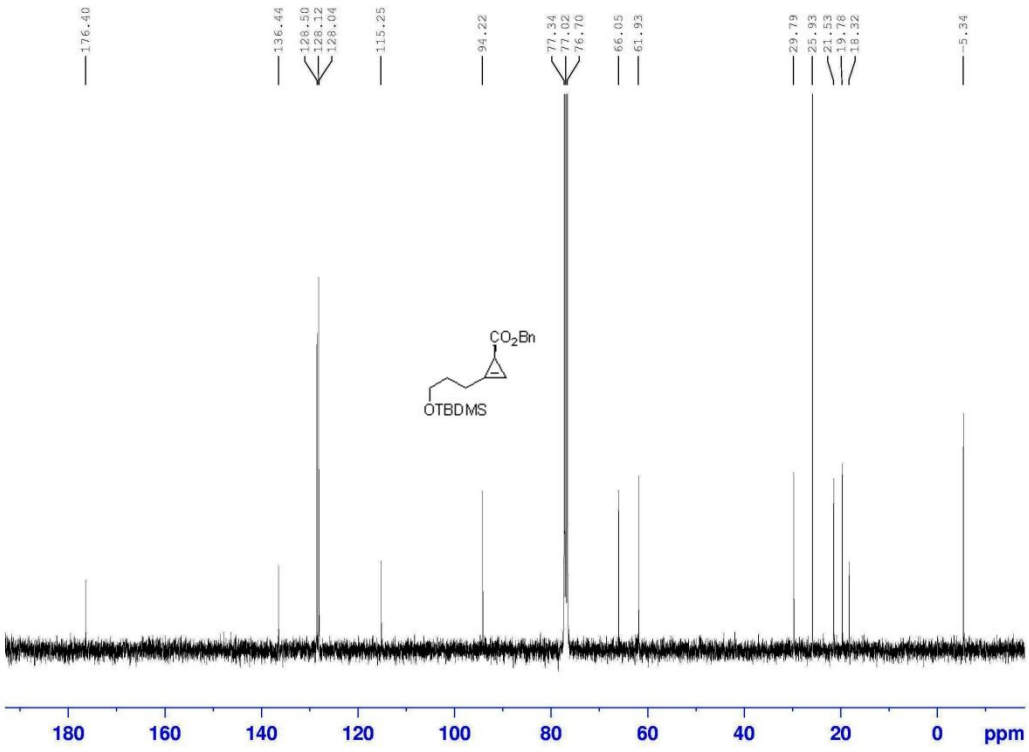
Results obtained with enhanced integrator!

*** End of Report ***

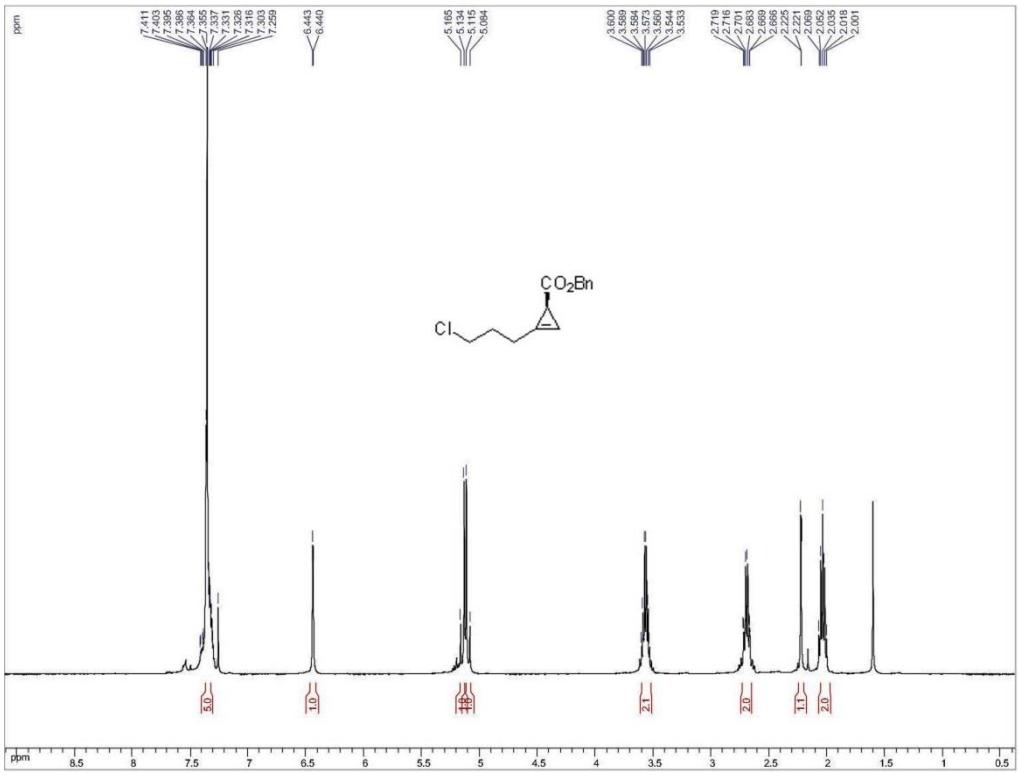
^{1}H NMR spectrum of 1g (400 MHz, $CDCl_3$):



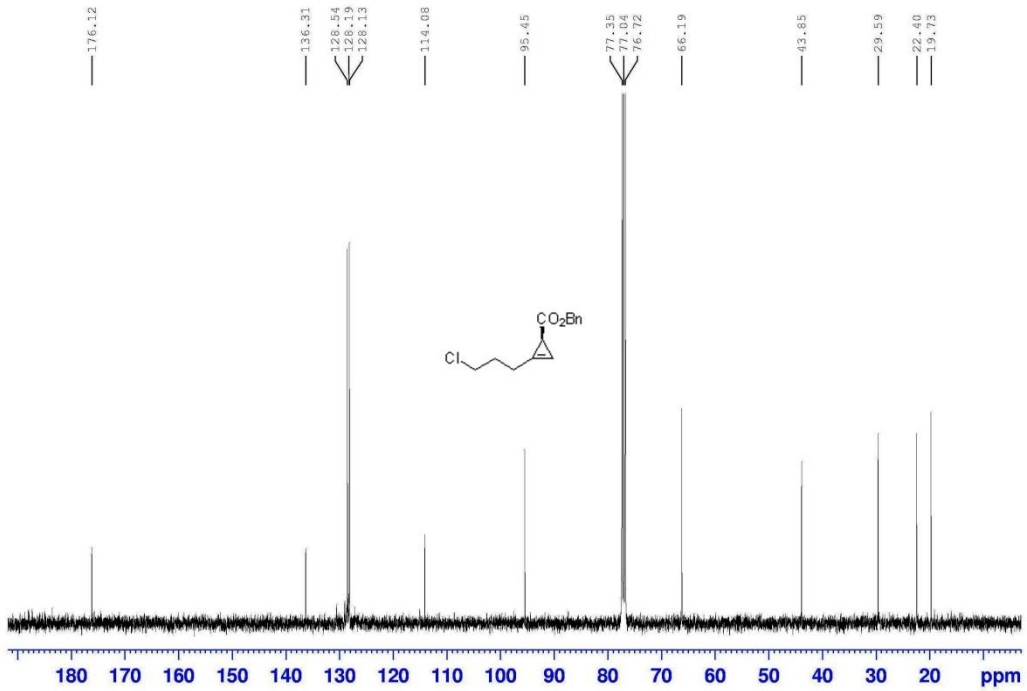
^{13}C NMR spectrum of 1g (100 MHz, $CDCl_3$):



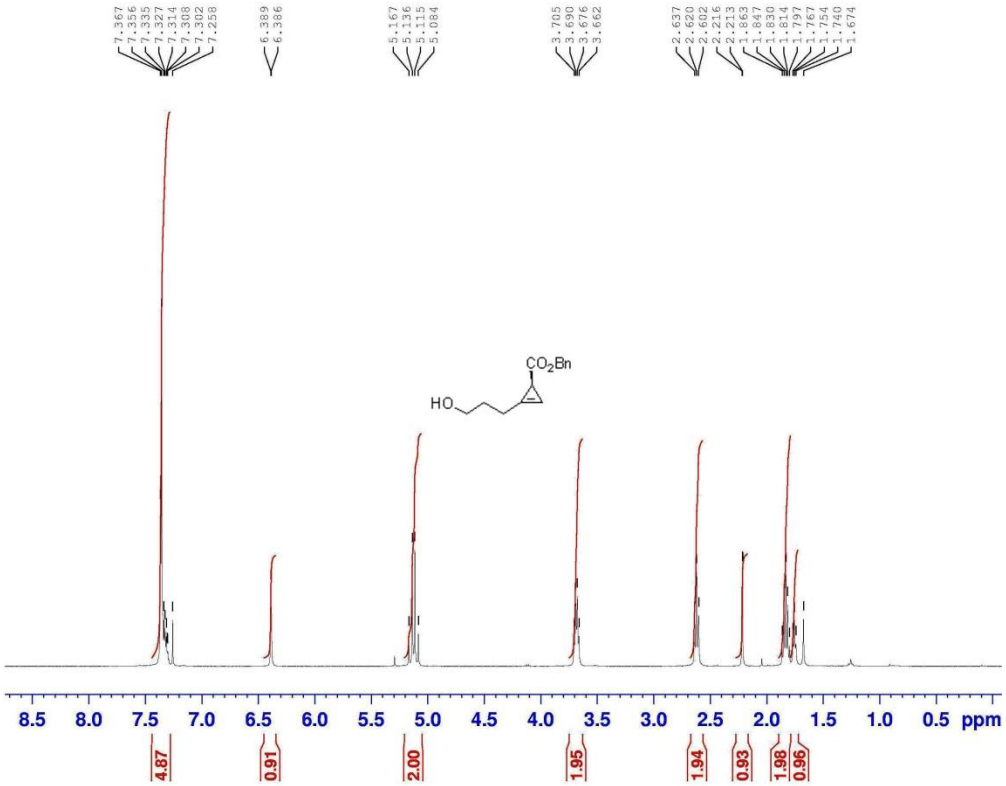
^{1}H NMR spectrum of 1h (400 MHz, $CDCl_3$):



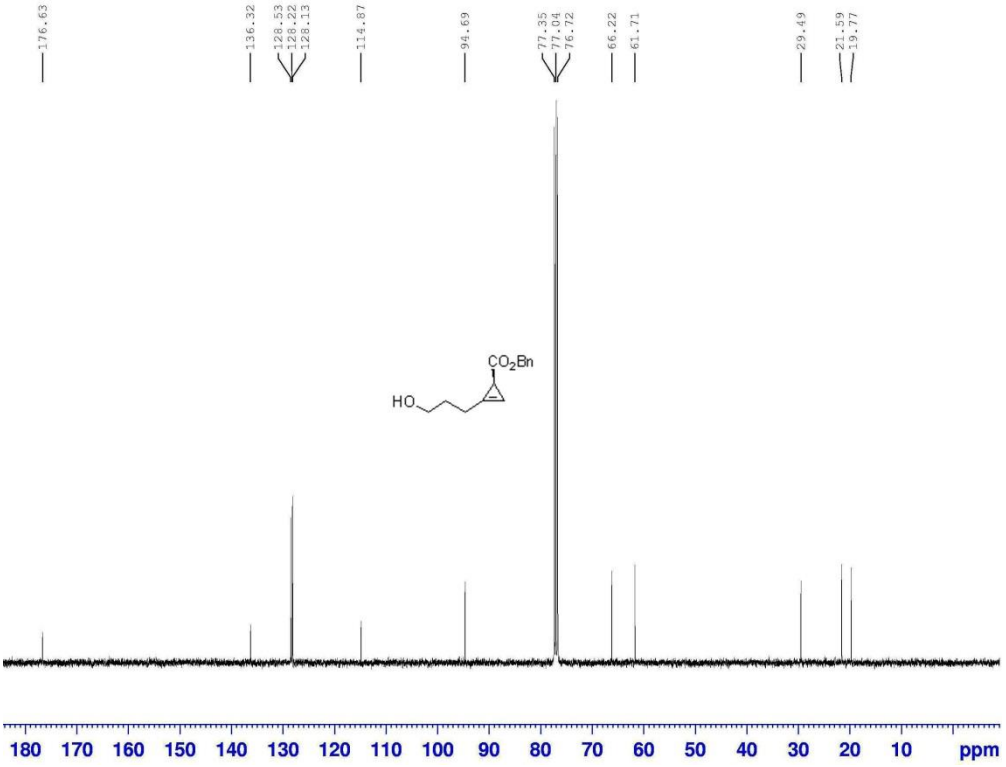
^{13}C NMR spectrum of 1h (100 MHz, $CDCl_3$):



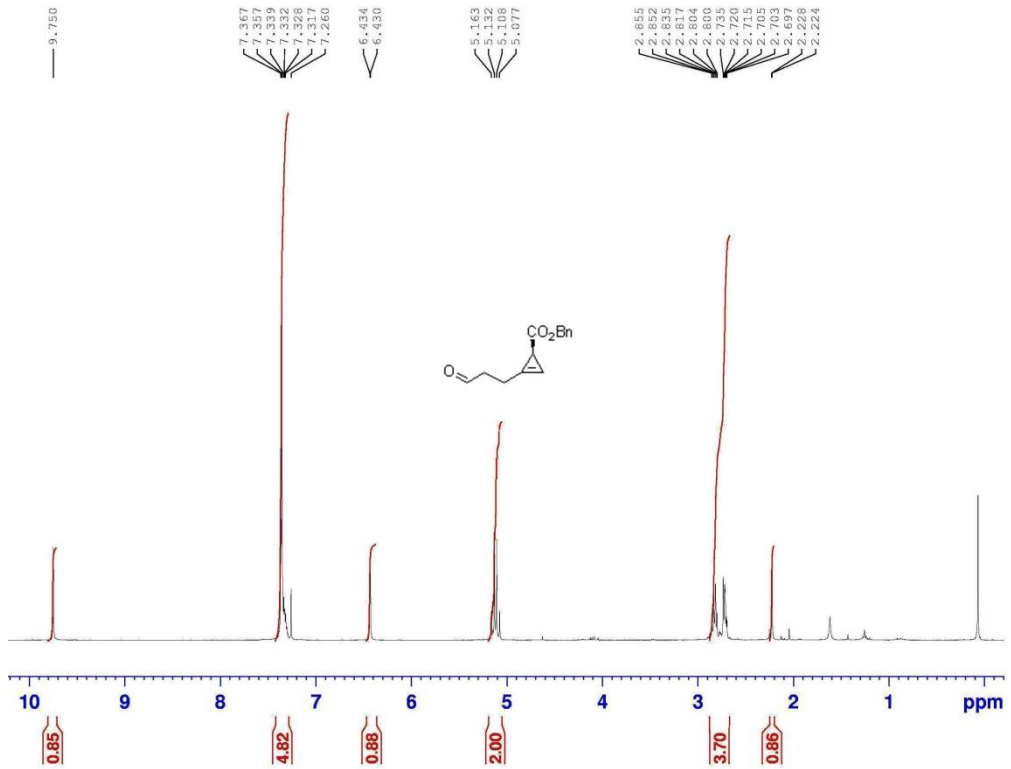
^{1}H NMR spectrum of 1ga (400 MHz, $CDCl_3$):



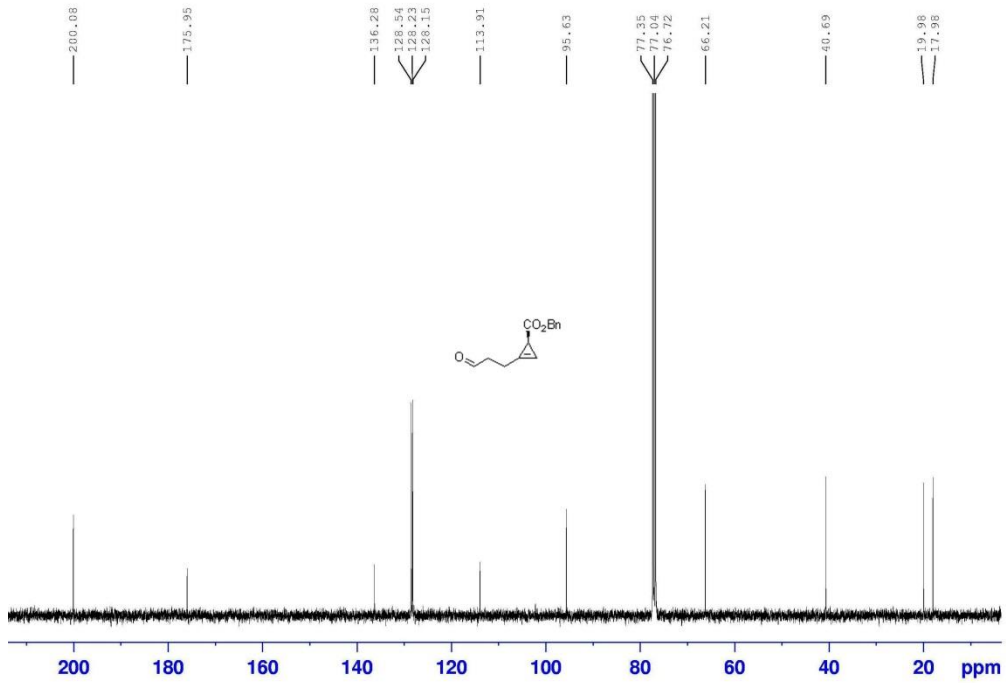
^{13}C NMR spectrum of 1ga (100 MHz, $CDCl_3$):



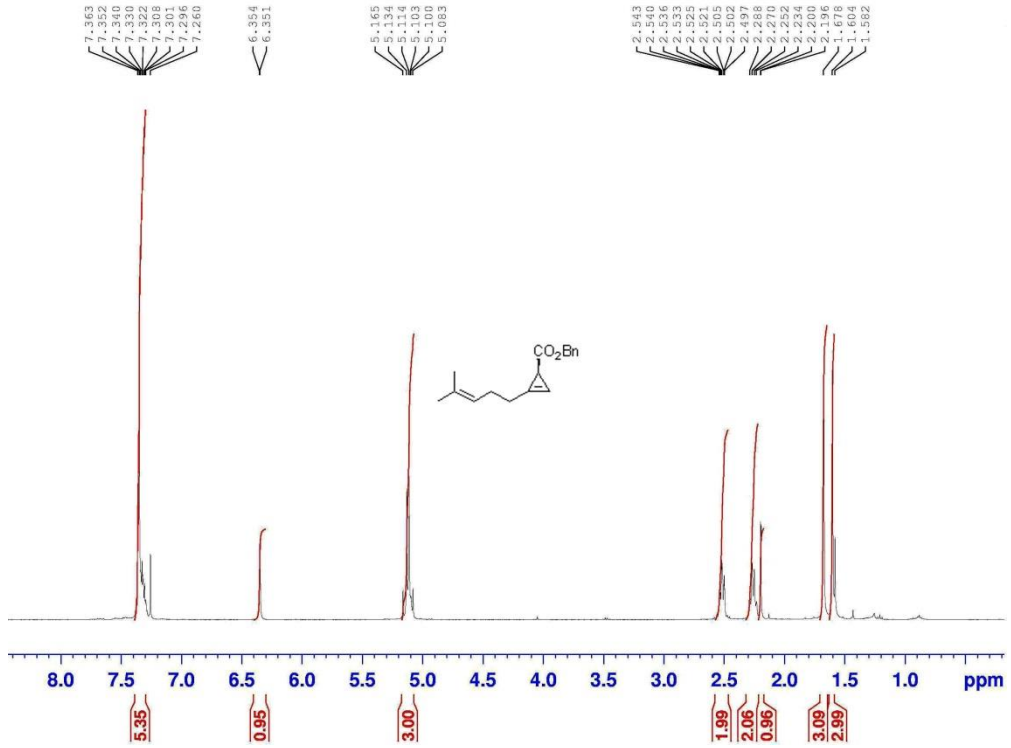
^{1}H NMR spectrum of 1gb (400 MHz, $CDCl_3$):



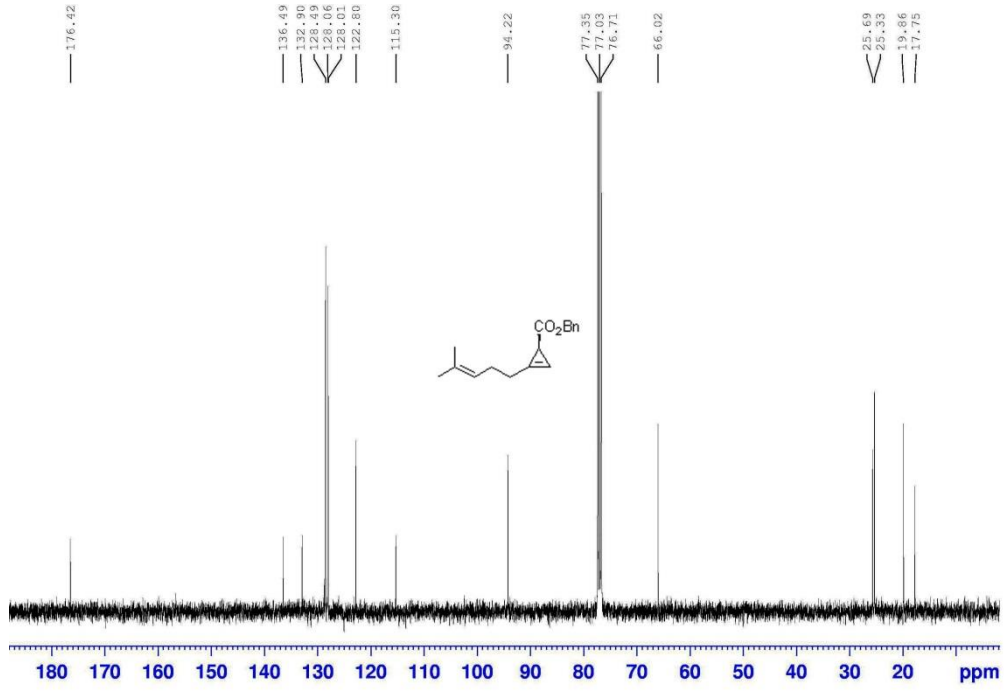
^{13}C NMR spectrum of 1gb (100 MHz, $CDCl_3$):



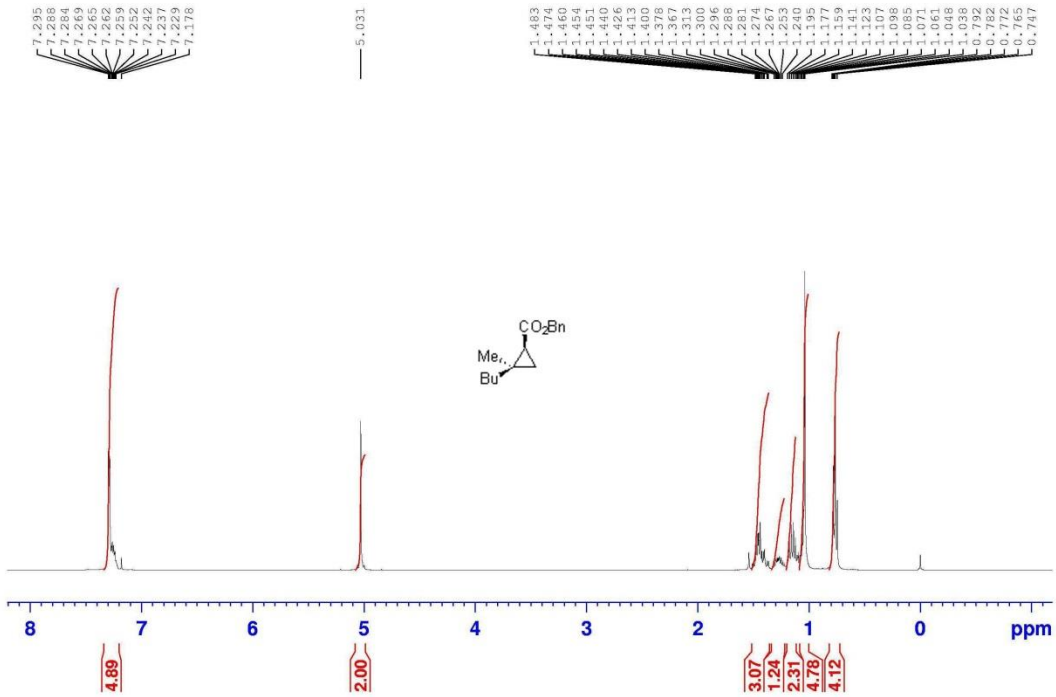
^{1}H NMR spectrum of 1i (400 MHz, $CDCl_3$):



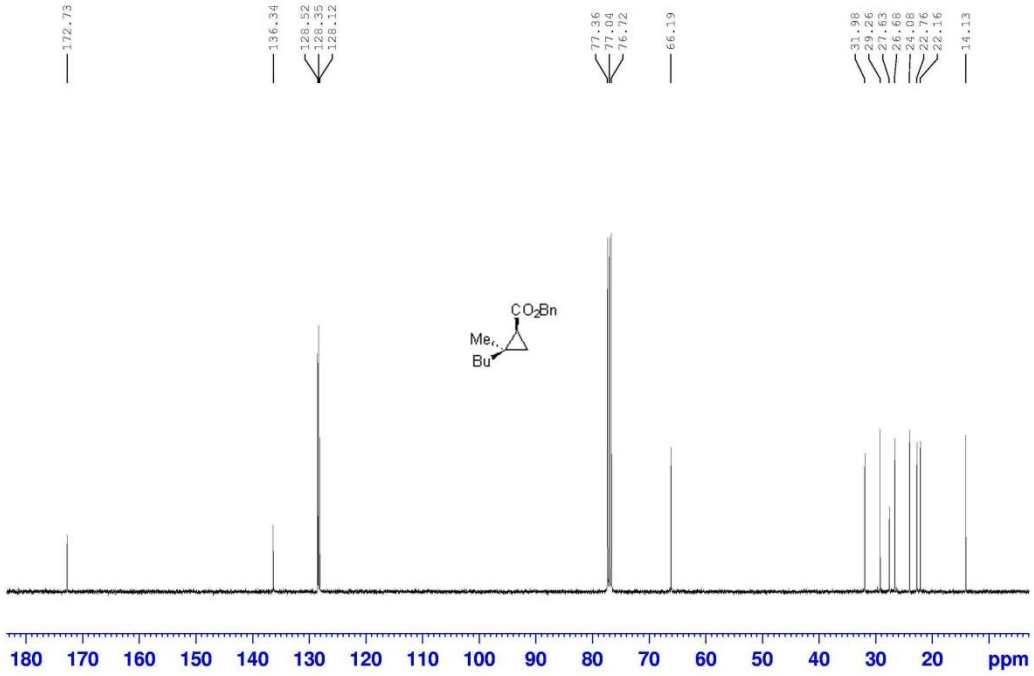
^{13}C NMR spectrum of 1i (100 MHz, $CDCl_3$):



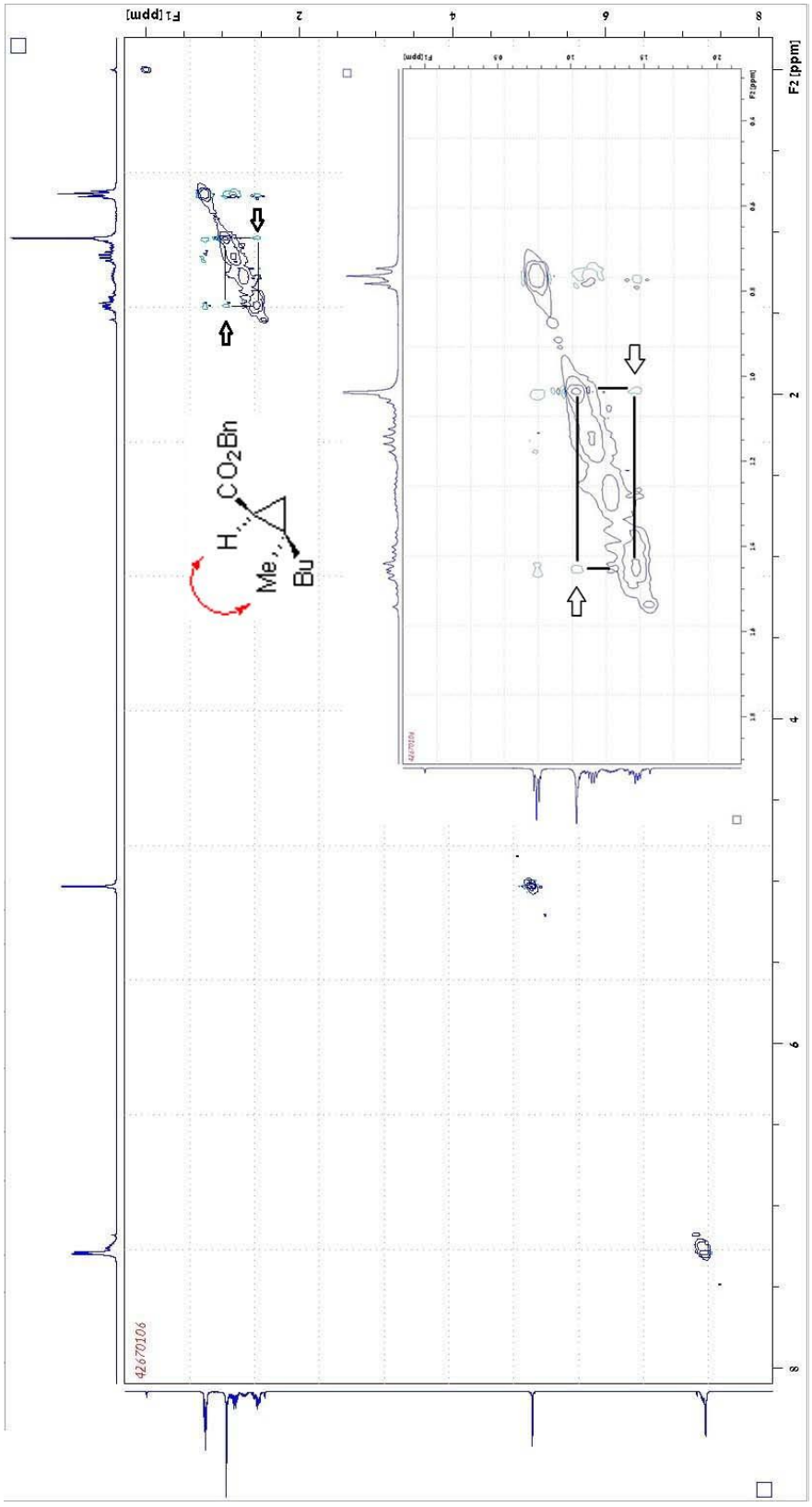
^{1}H NMR spectrum of 2a$_{anti}$ (400 MHz, $CDCl_3$):



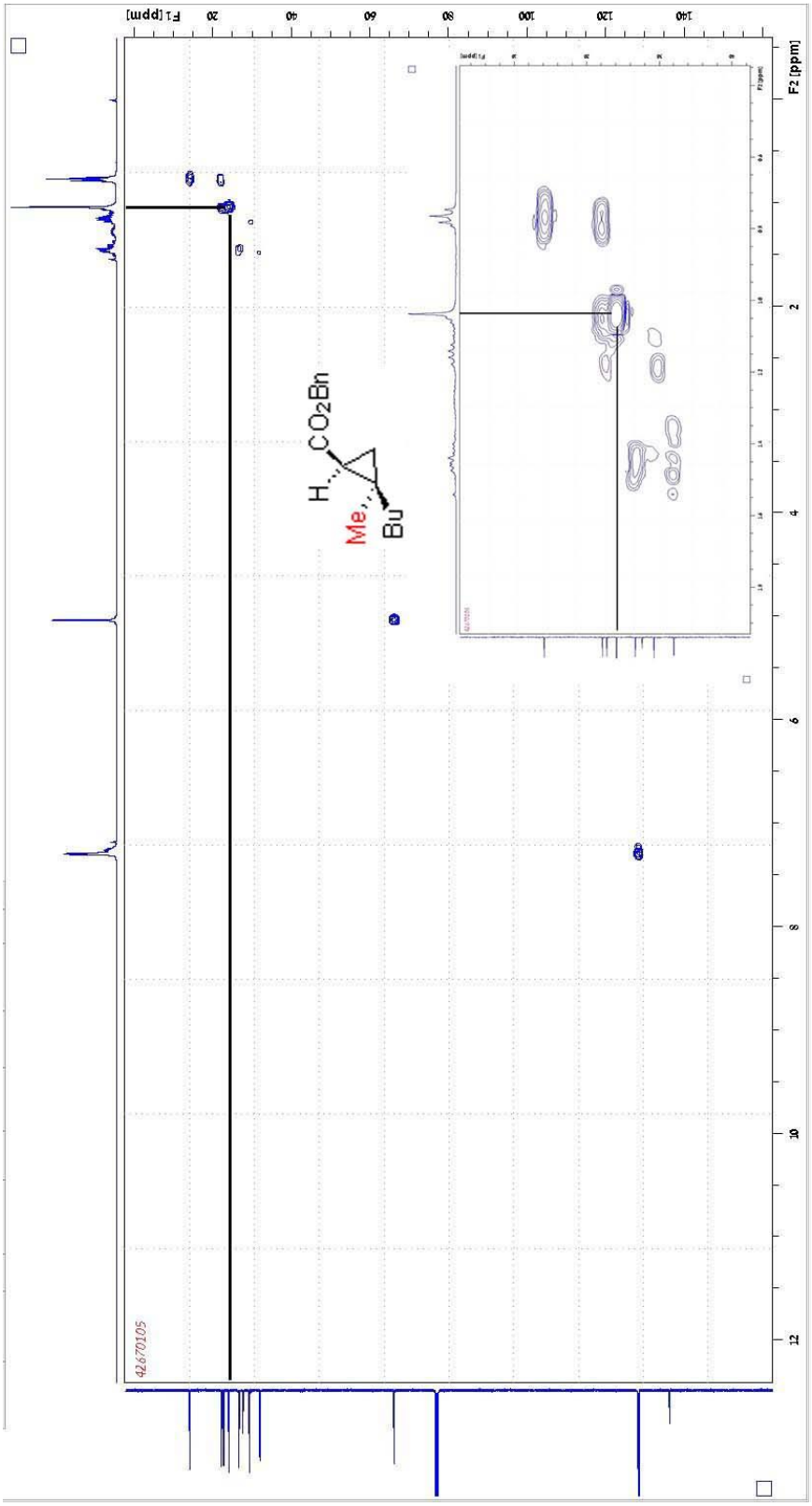
^{13}C NMR spectrum of 2a$_{anti}$ (100 MHz, $CDCl_3$):



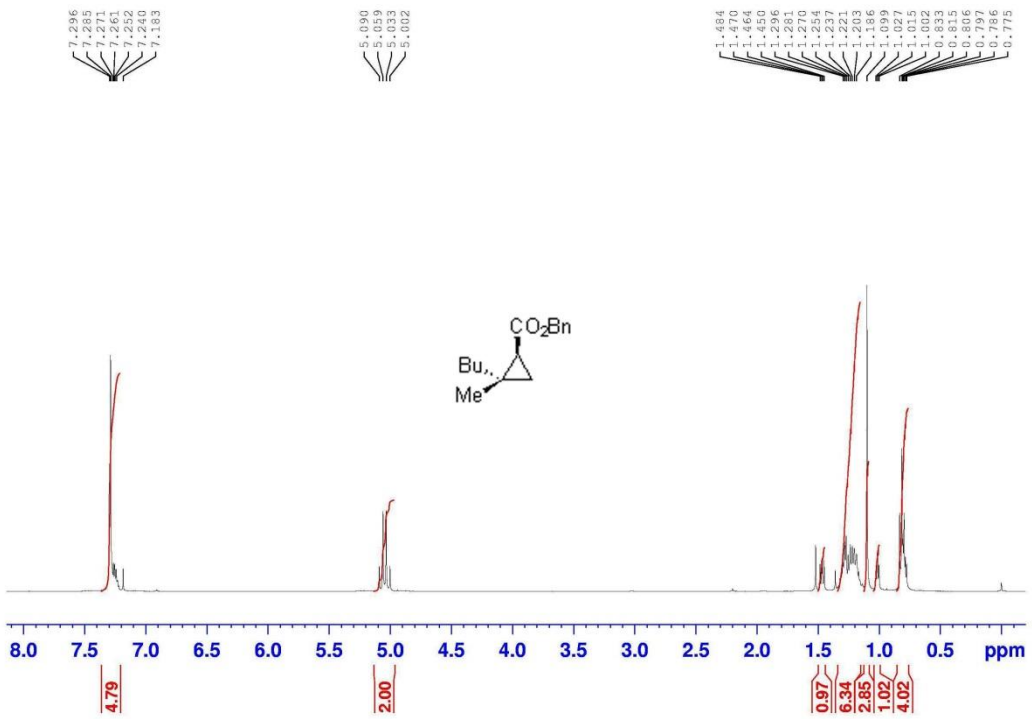
^{1}H-^{1}H NOESY spectrum of 2a$_{anti}$ (400 MHz, $CDCl_3$):



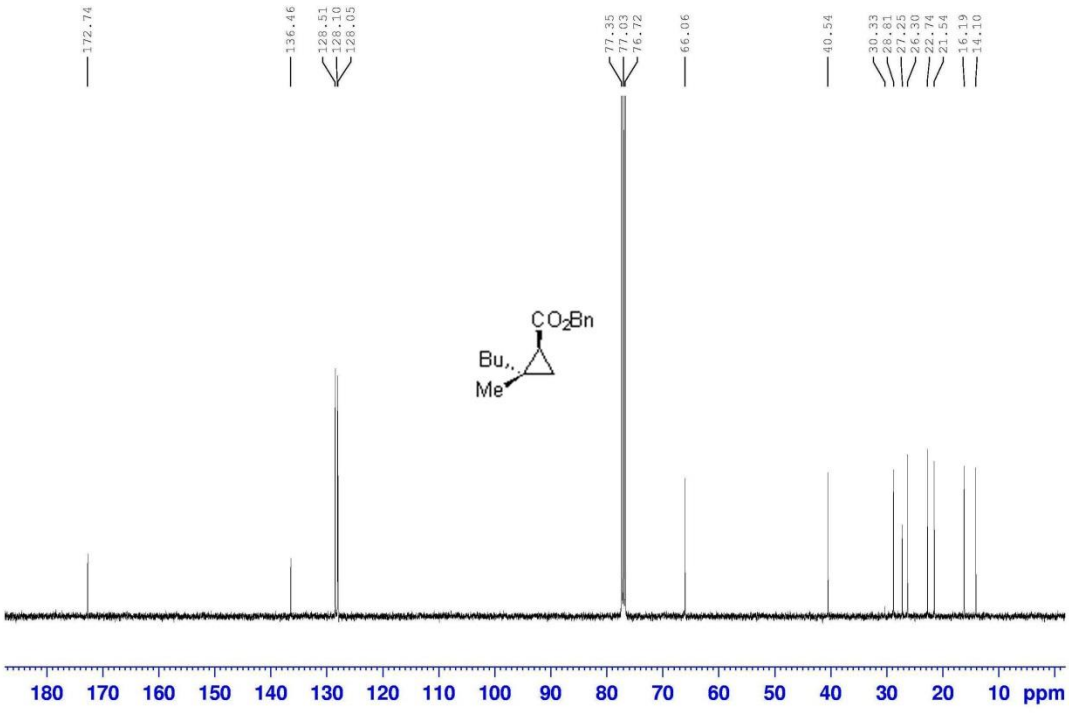
HMQC spectrum of 2a$_{anti}$:



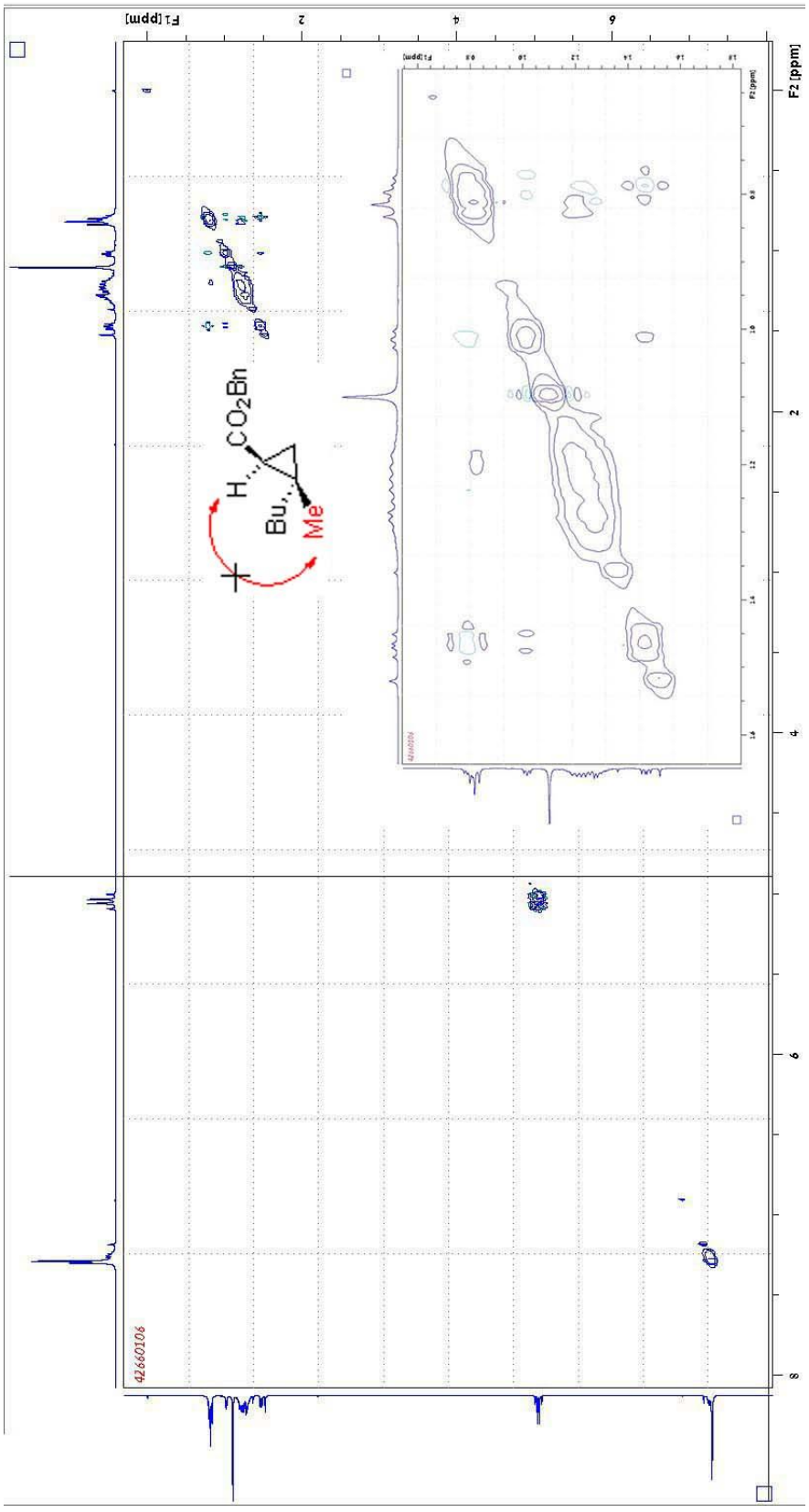
^{1}H NMR spectrum of 2a$_{syn}$ (400 MHz, $CDCl_3$):



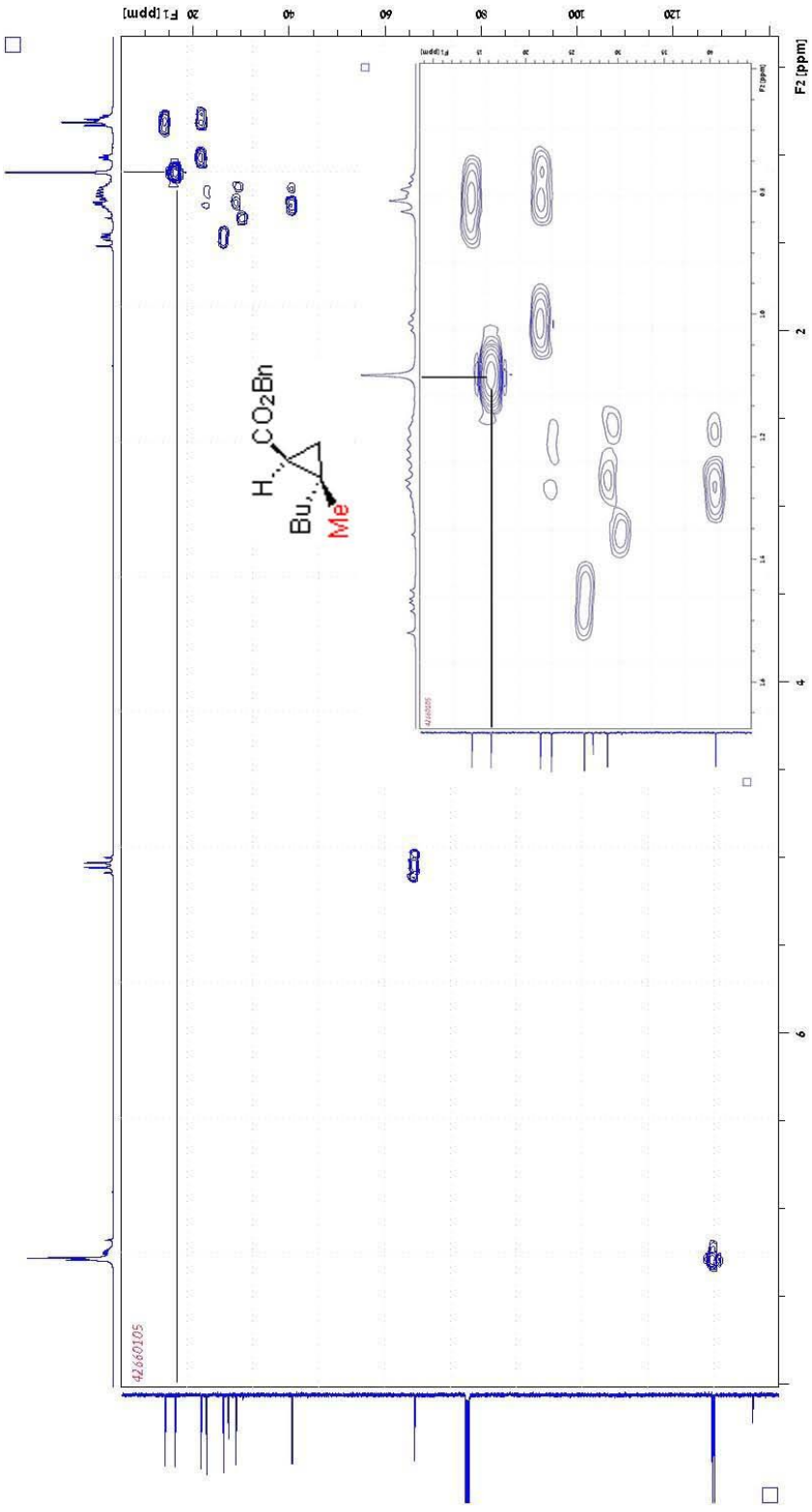
^{13}C NMR spectrum of 2a$_{syn}$ (100 MHz, $CDCl_3$):



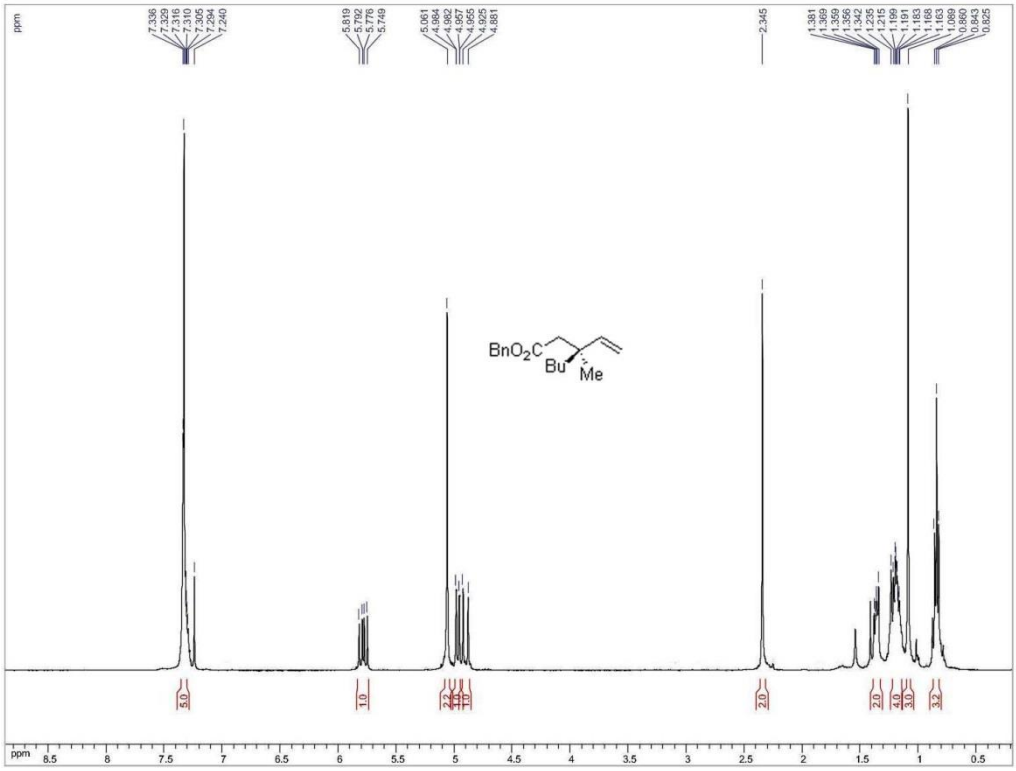
^{1}H-^{1}H NOESY spectrum of 2a$_{syn}$ (400 MHz, $CDCl_3$):



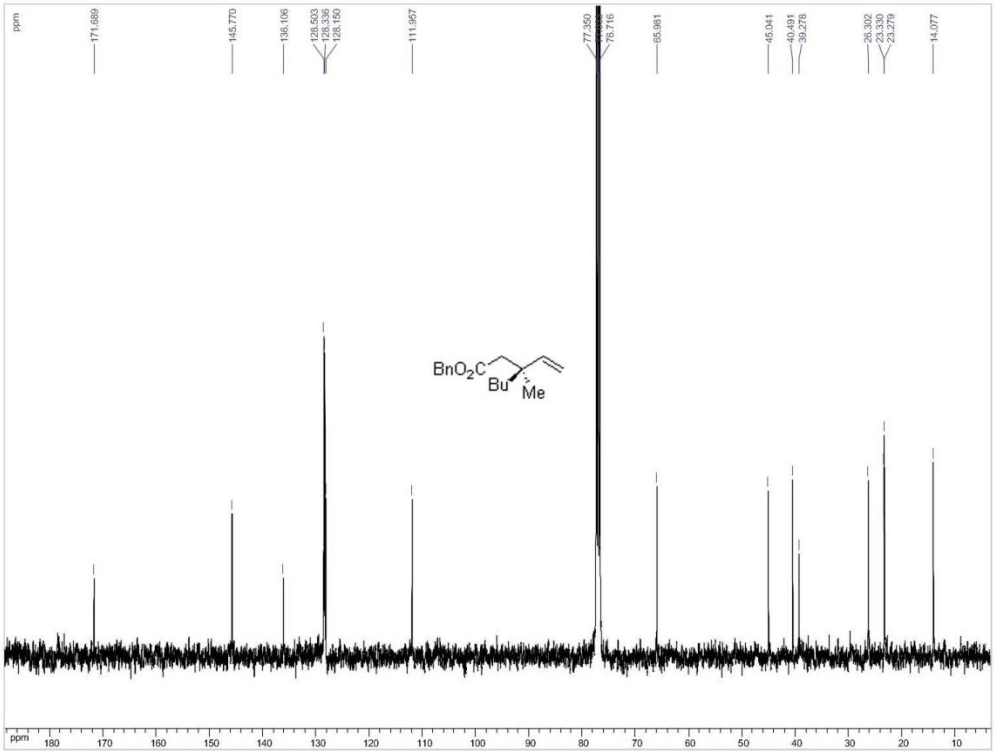
HMQC spectrum of 2a$_{syn}$:



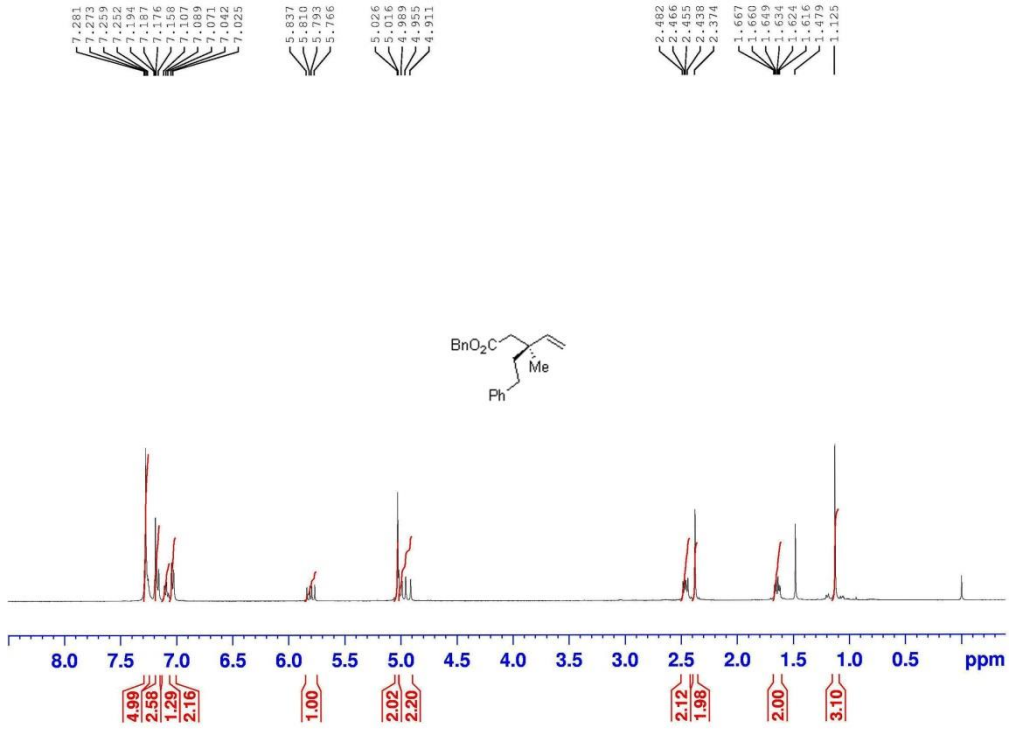
^{1}H NMR spectrum of 4a (400 MHz, $CDCl_3$):



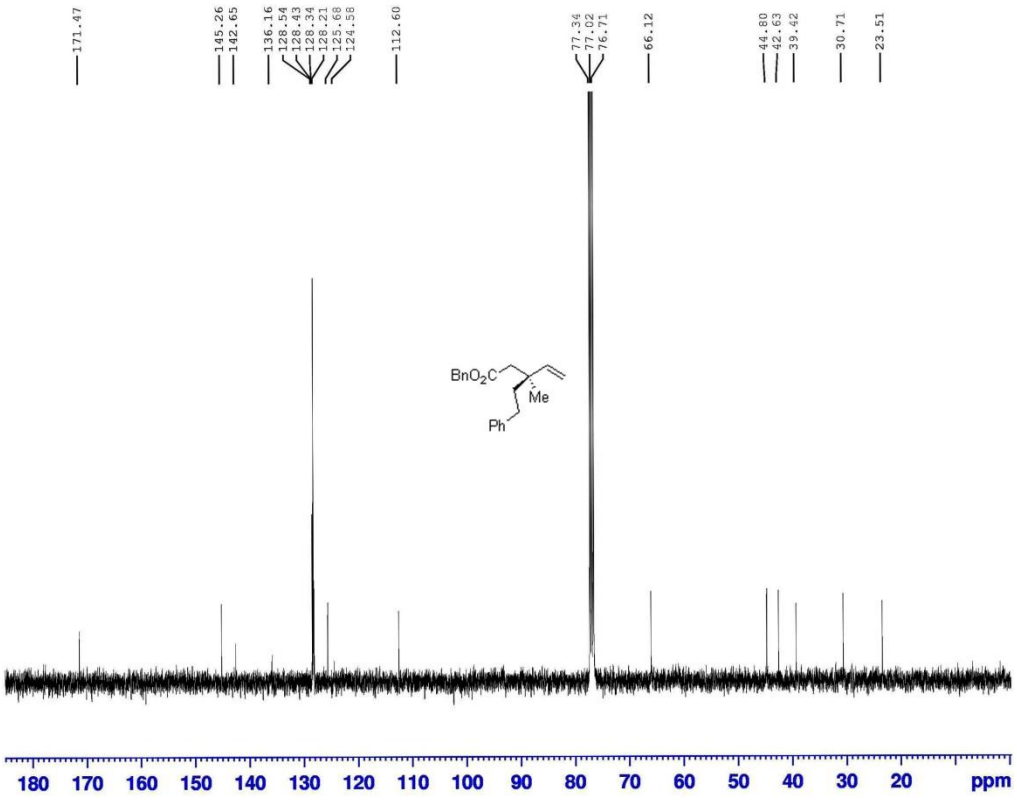
^{13}C NMR spectrum of 4a (100 MHz, $CDCl_3$):



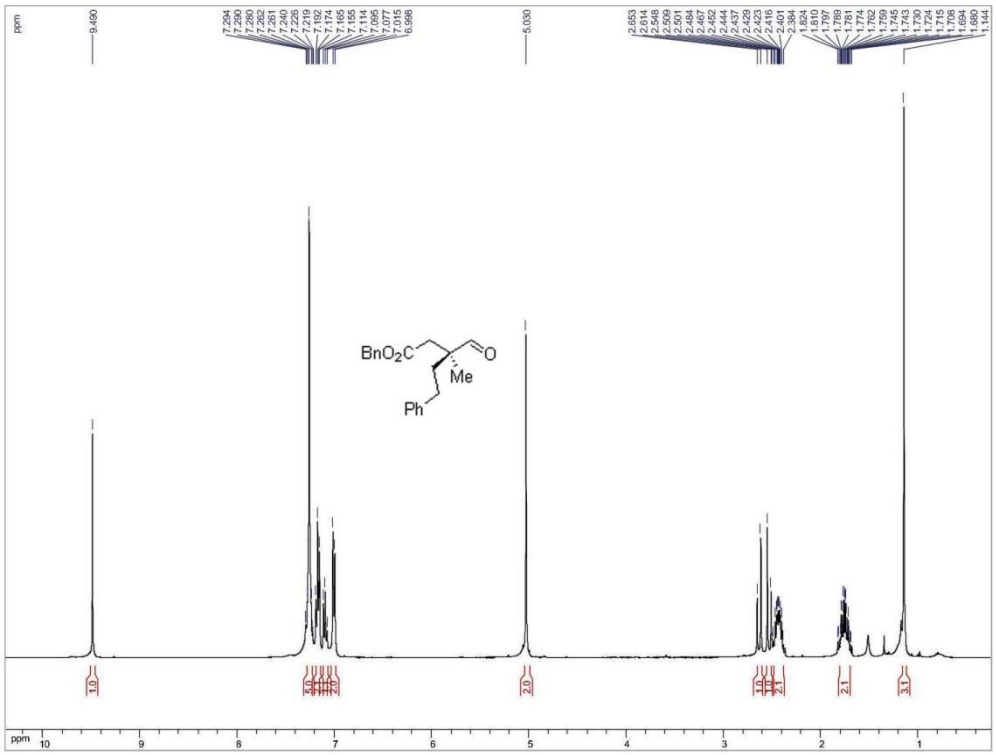
^{1}H NMR spectrum of 4b (400 MHz, $CDCl_3$):



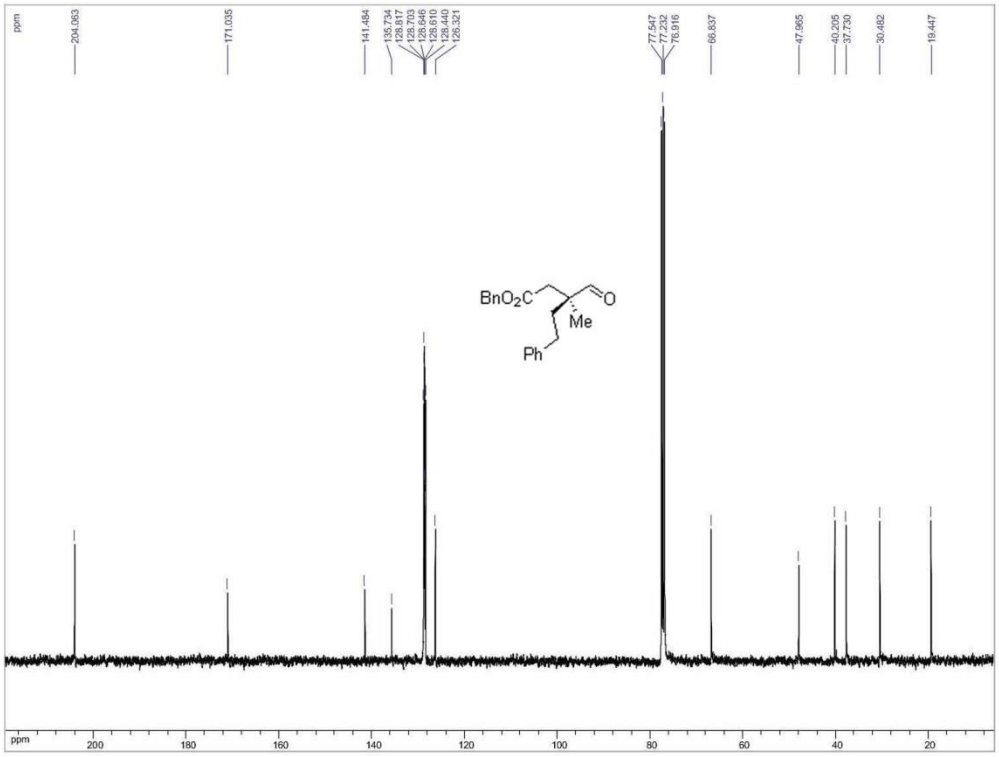
^{13}C NMR spectrum of 4b (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of 5b (400 MHz, $CDCl_3$):

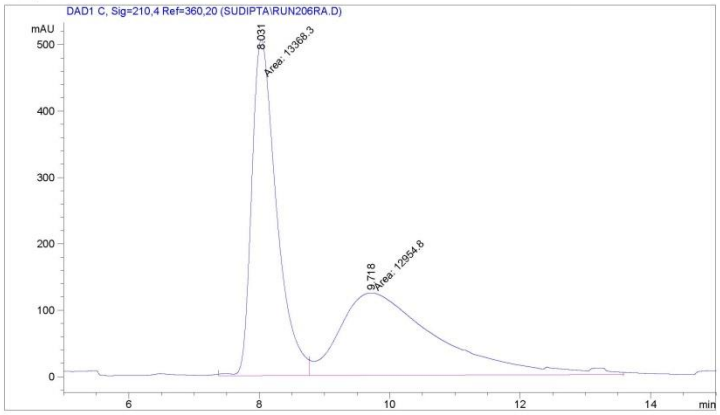


^{13}C NMR spectrum of 5b (100 MHz, $CDCl_3$):



HPLC analysis of the racemic and enantioenriched 5b:

AY-H
Hex:IPA = 90:10
1 mL/min

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Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.031 MF    0.4403 1.33683e4   505.99207  50.7855
   2   9.718 FM    1.7388 1.29548e4   124.17191  49.2145

Totals :                  2.63231e4   630.16397

 Results obtained with enhanced integrator!
=====================================================================
                      *** End of Report ***
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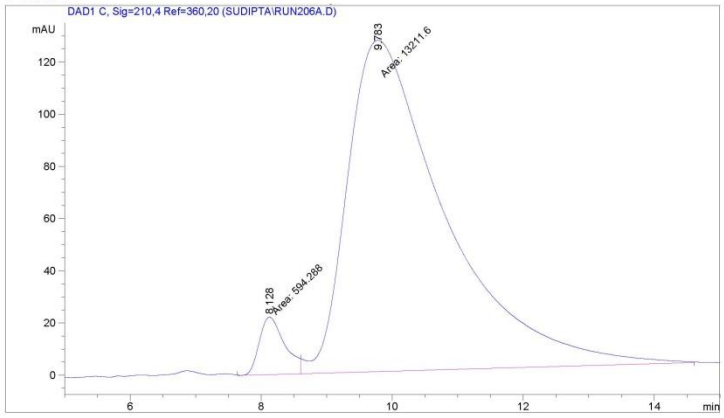
AY-H
Hex:IPA = 90:10
1 mL/min

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=====================================================================
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Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

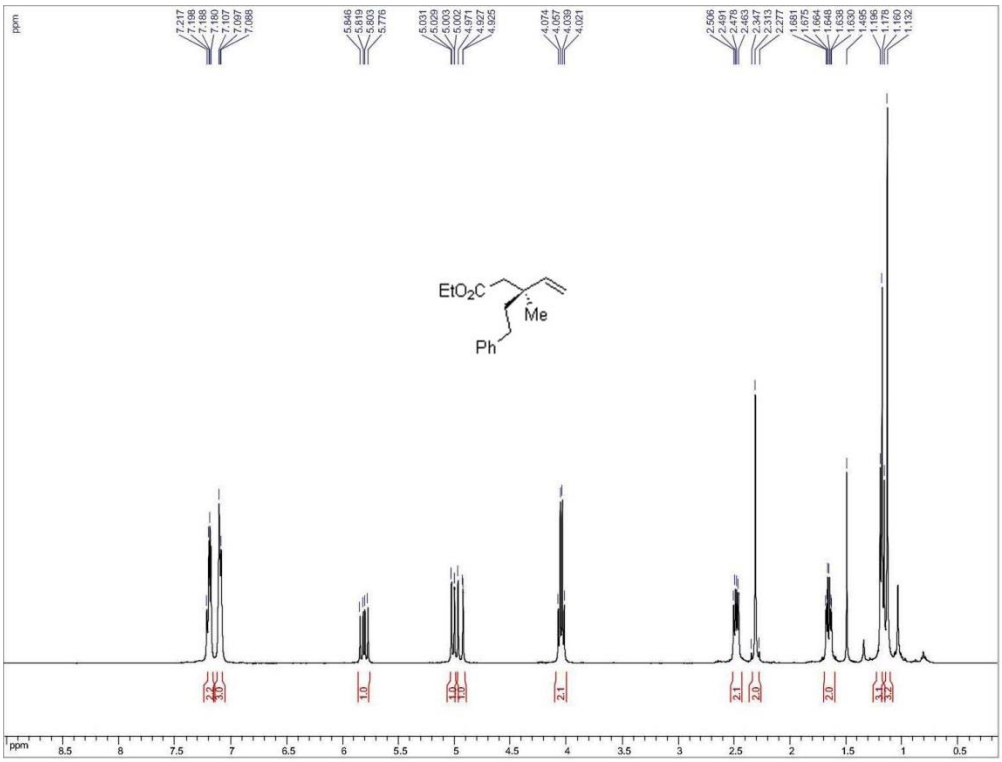

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.128 MF    0.4488  594.28772   22.06885   4.3046
   2   9.783 FM    1.7339 1.32116e4   126.99159  95.6954

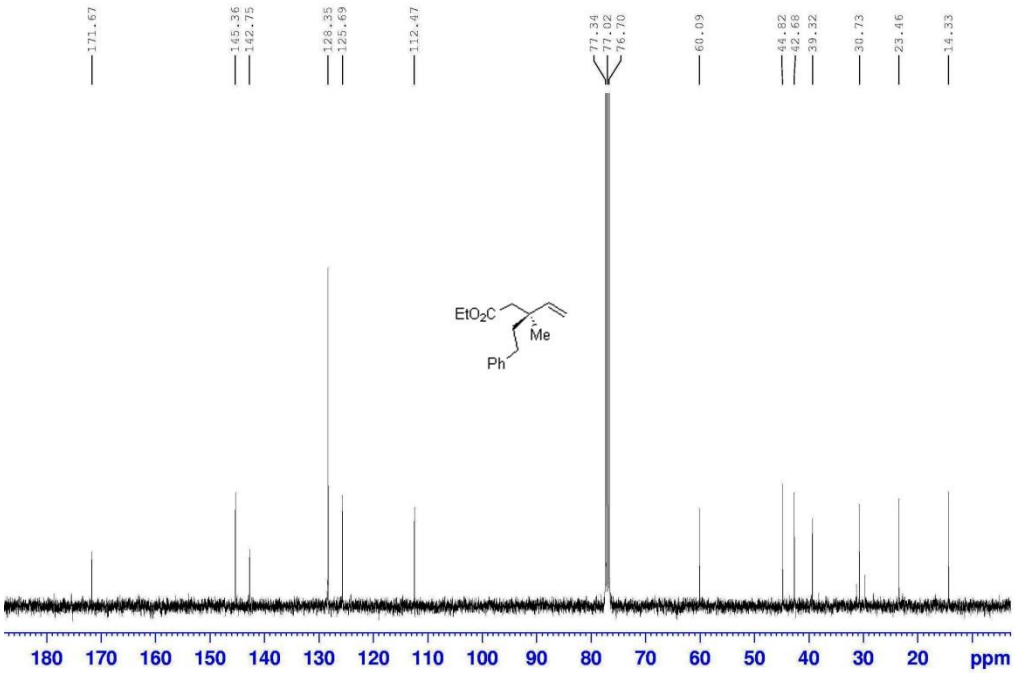
Totals :                  1.38059e4   149.06044

 Results obtained with enhanced integrator!
=====================================================================
                      *** End of Report ***
```

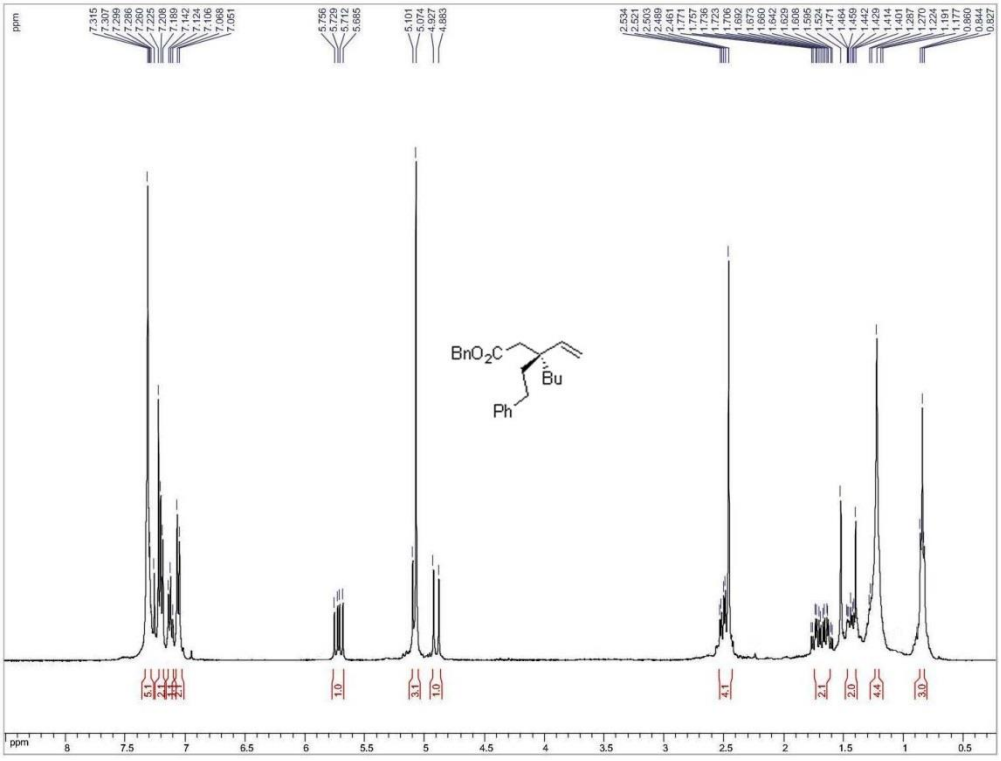
^{1}H NMR spectrum of 4c (400 MHz, $CDCl_3$):



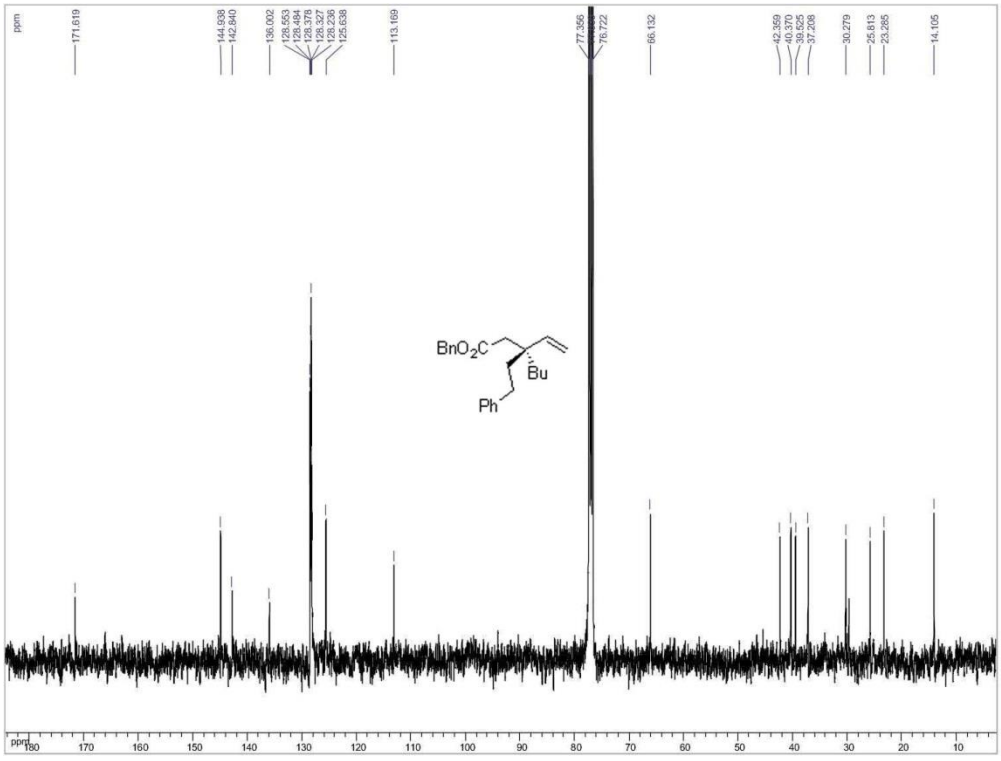
^{13}C NMR spectrum of 4c (100 MHz, $CDCl_3$):



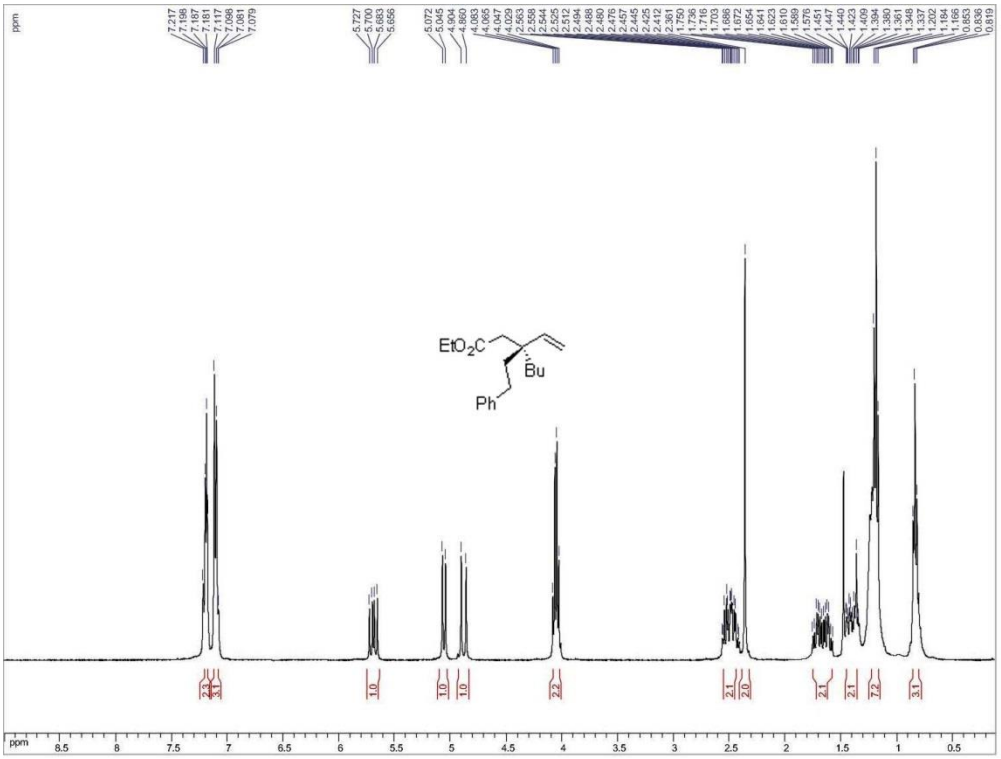
^{1}H NMR spectrum of 4d (400 MHz, $CDCl_3$):



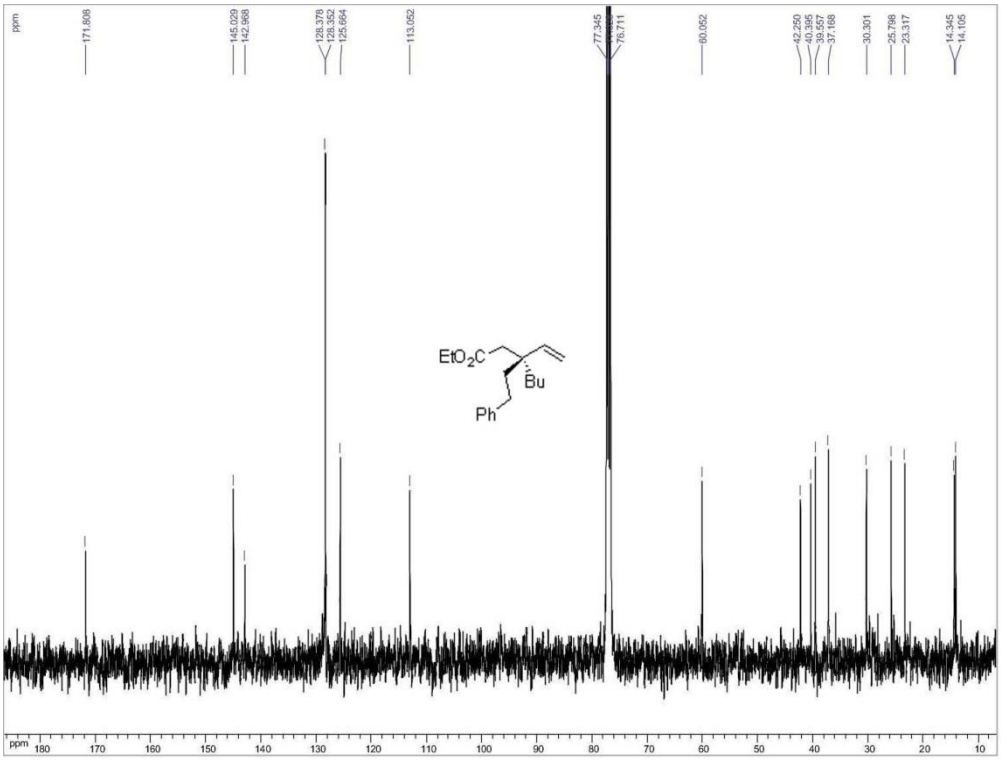
^{13}C NMR spectrum of 4d (100 MHz, $CDCl_3$):



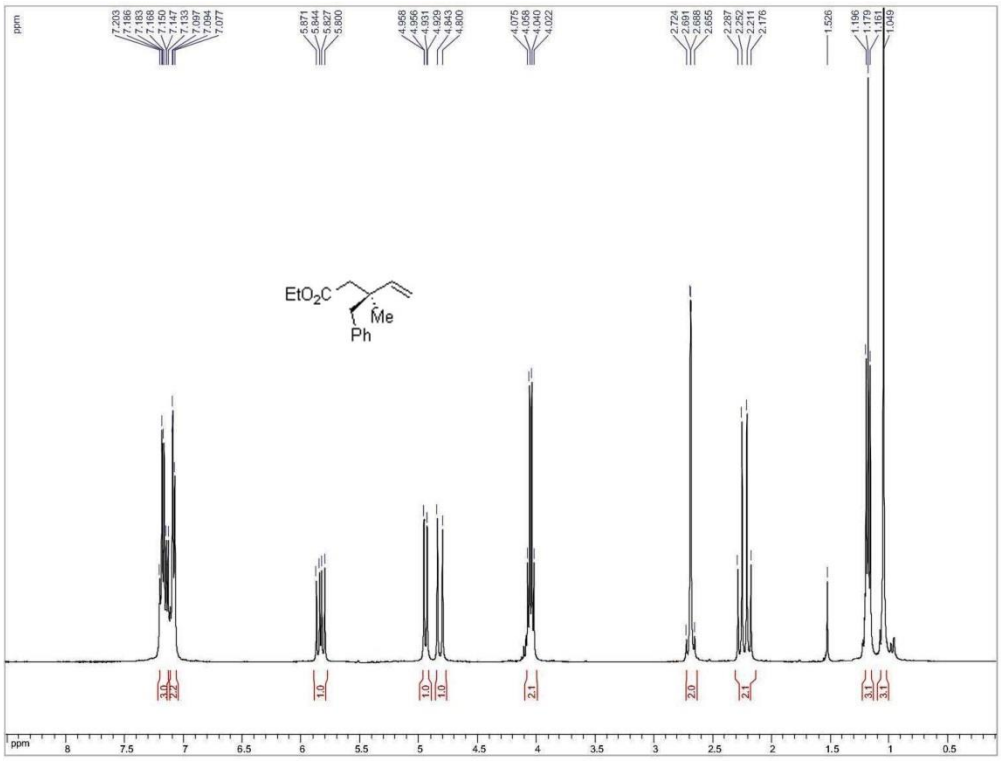
^{1}H NMR spectrum of 4e (400 MHz, $CDCl_3$):



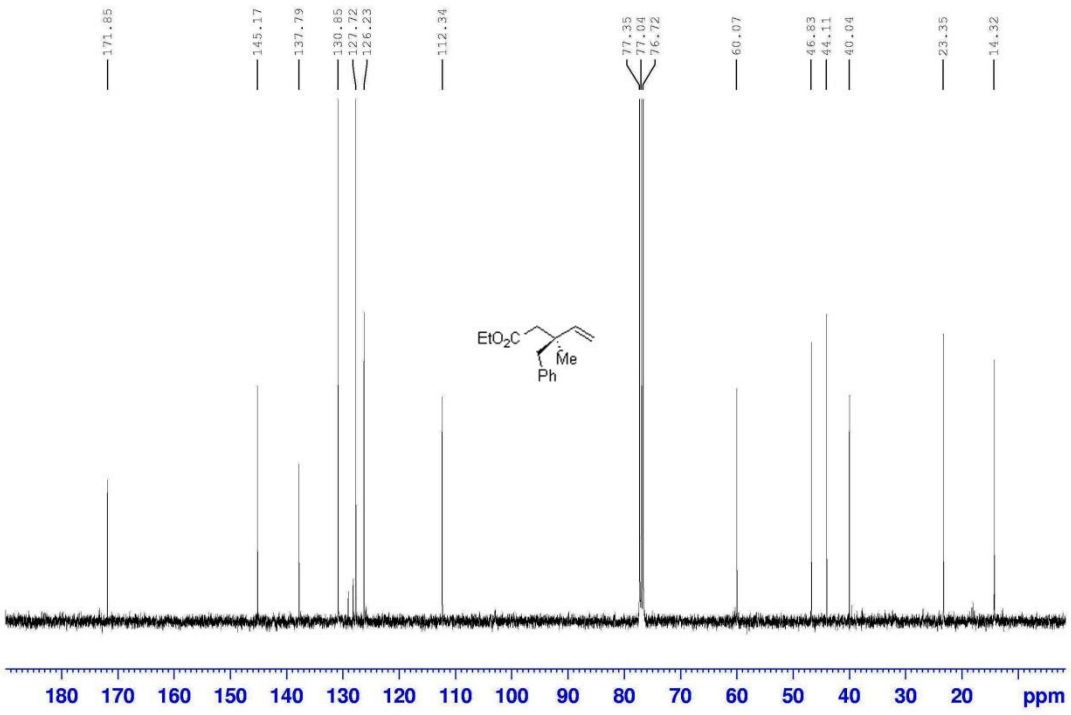
^{13}C NMR spectrum of 4e (100 MHz, $CDCl_3$):



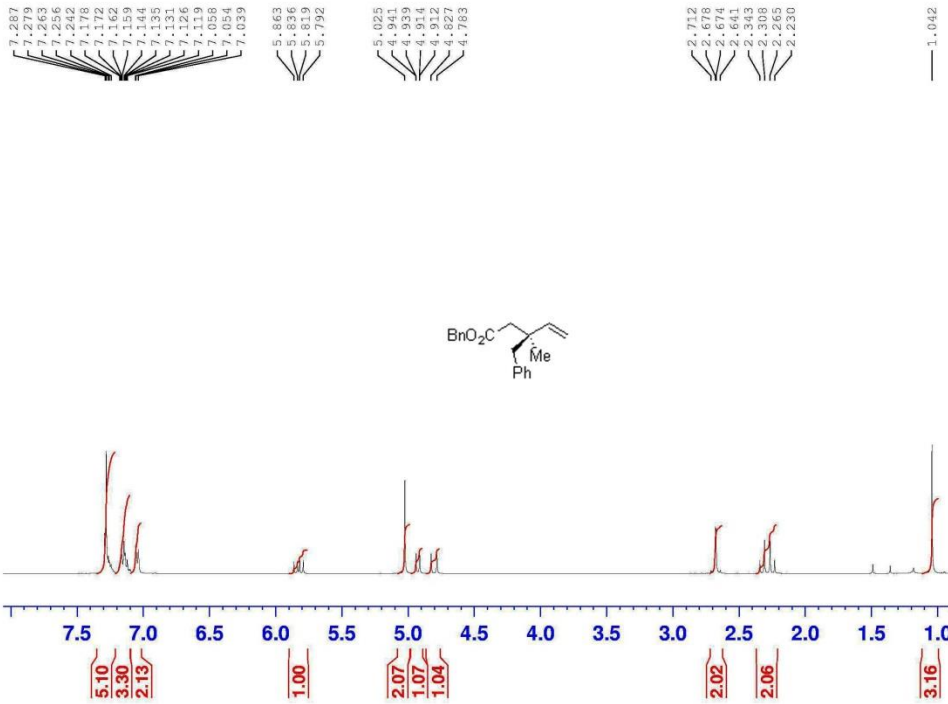
^{1}H NMR spectrum of 4f (400 MHz, $CDCl_3$):



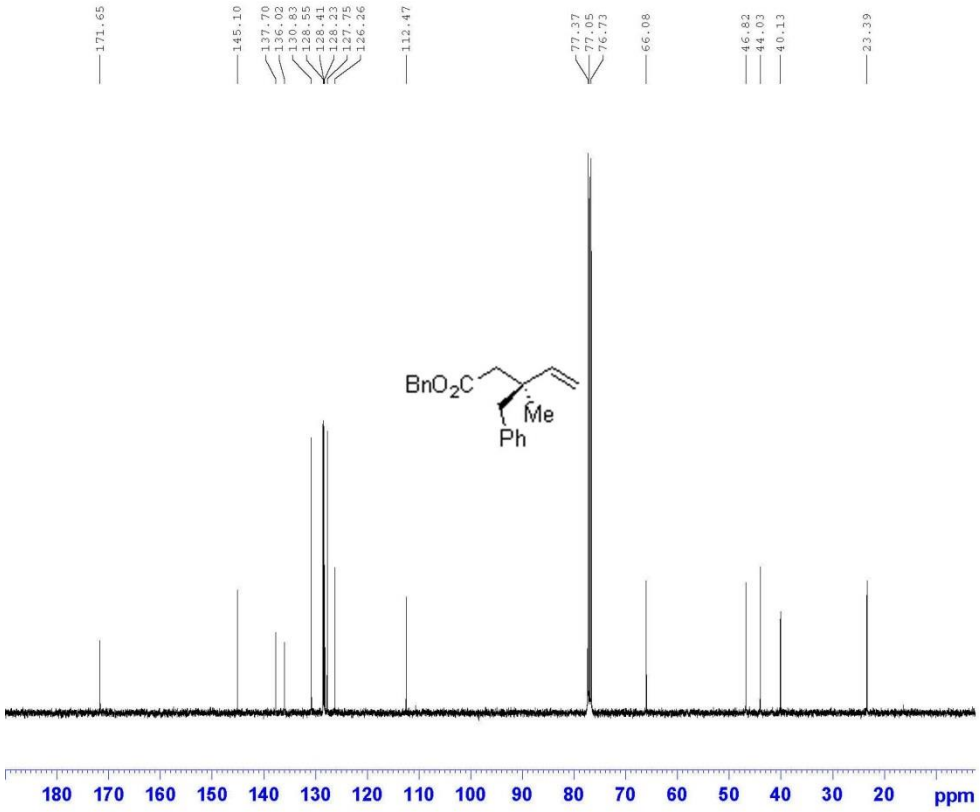
^{13}C NMR spectrum of 4f (100 MHz, $CDCl_3$):



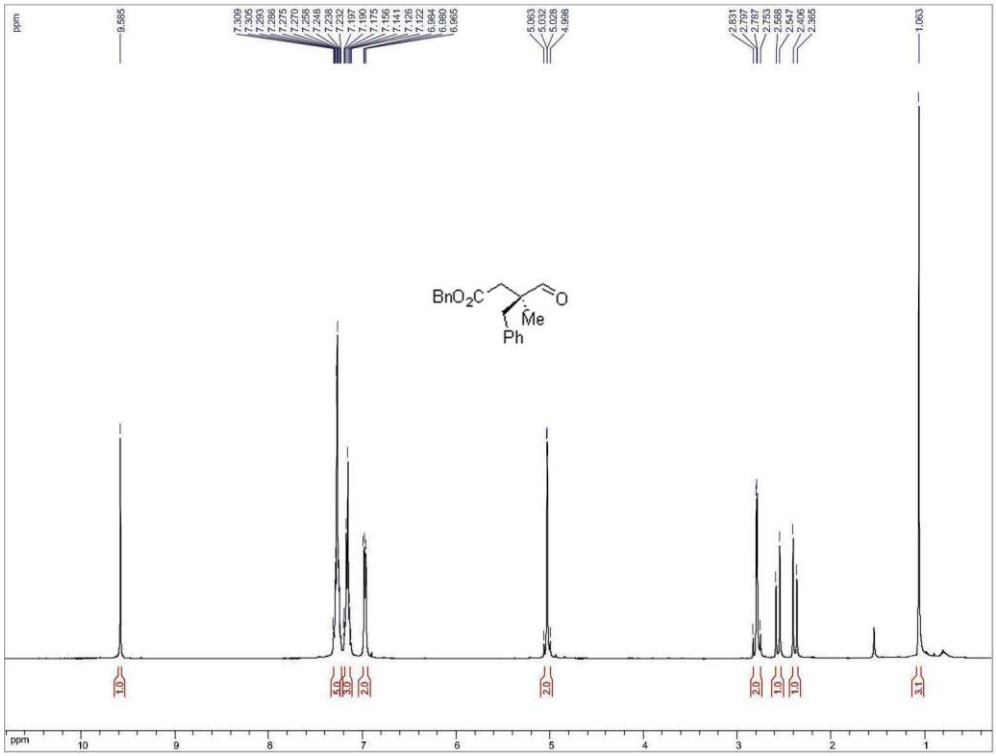
^{1}H NMR spectrum of 4g (400 MHz, $CDCl_3$):



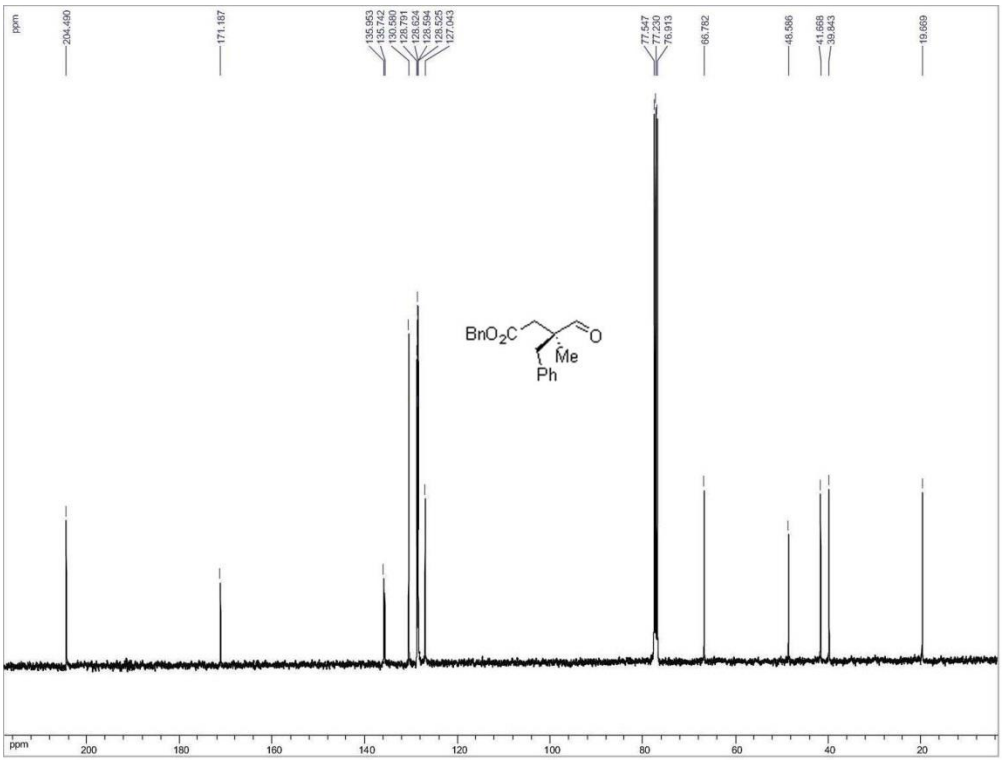
^{13}C NMR spectrum of 4g (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of 5g (400 MHz, $CDCl_3$):

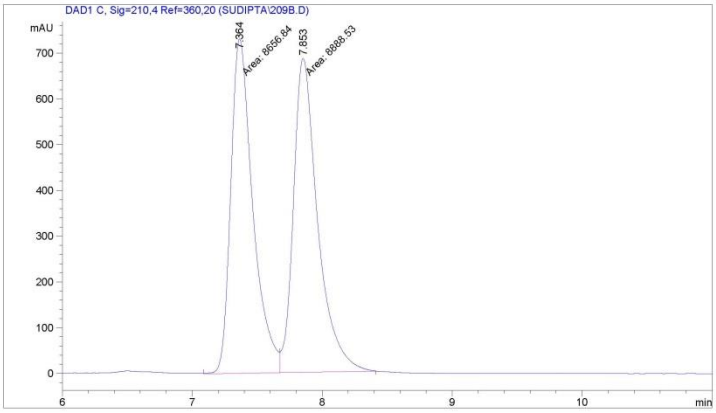


^{13}C NMR spectrum of 5g (100 MHz, $CDCl_3$):



HPLC analysis of the racemic and enantioenriched 5g:

AD-H
Hex/iPrOH = 90:10
1 mL/min

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Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1   7.364 MF    0.1971 8656.84473  731.97760  49.3398
   2   7.853 FM    0.2157 8888.52734  686.72626  50.6602

Totals :                  1.75454e4  1418.70386

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
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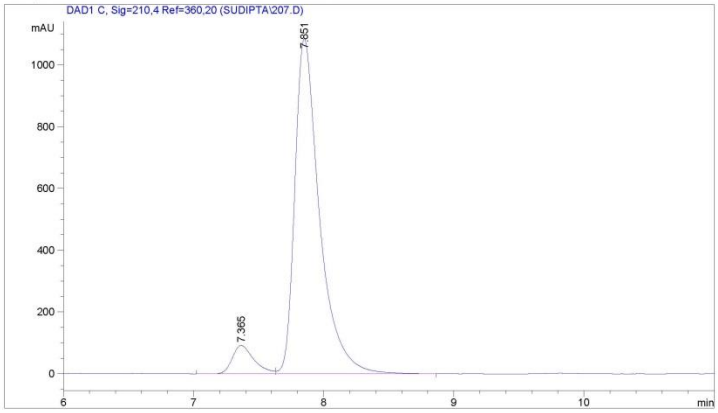
AD-H
Hex/iPrOH = 90:10
1 mL/min

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================================================================================
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1   7.365 BV    0.1754 1071.15564   92.29800   6.9485
   2   7.851 VB    0.1962 1.43445e4  1085.33301  93.0515

Totals :                  1.54157e4  1177.63101

 Results obtained with enhanced integrator!
================================================================================
                          *** End of Report ***
```
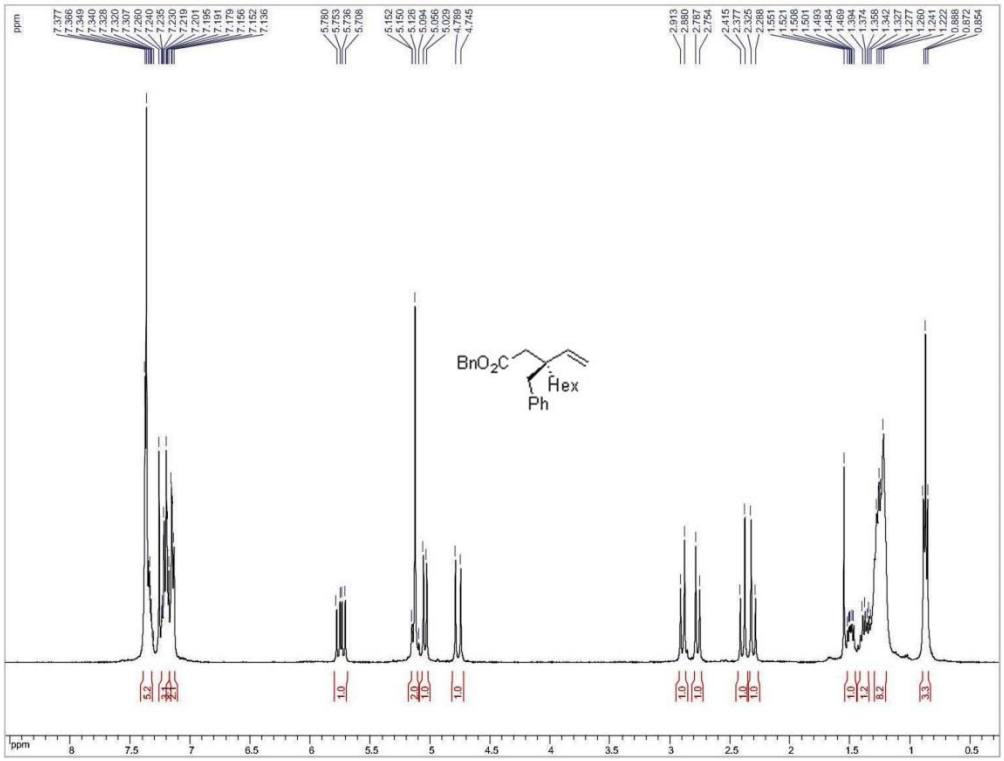
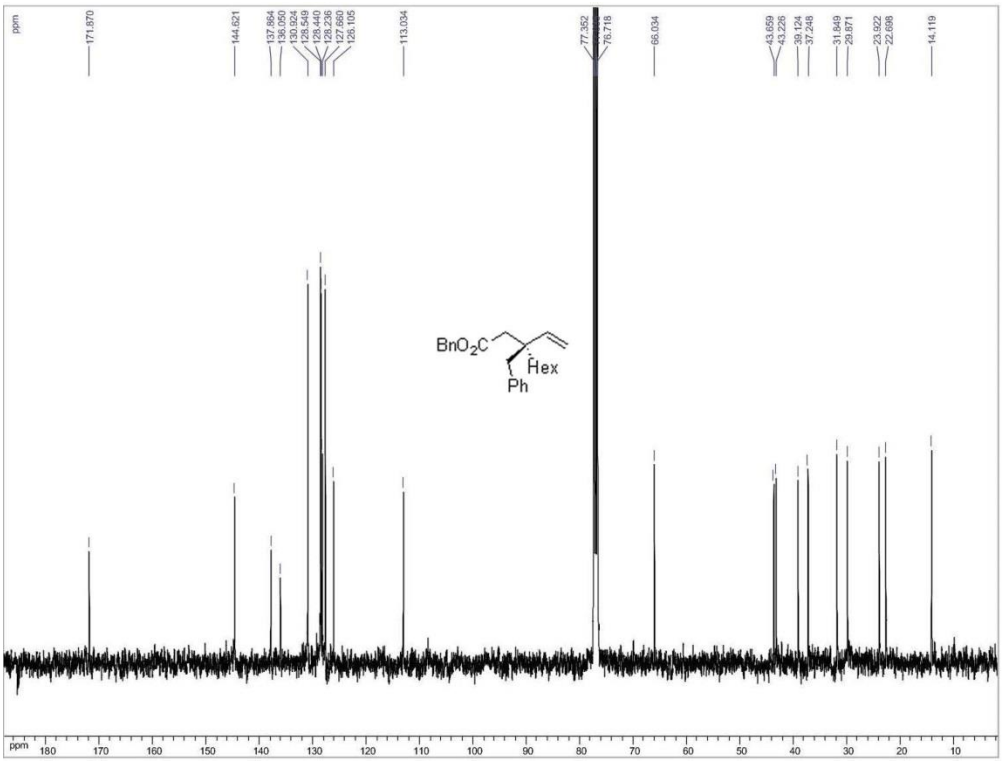
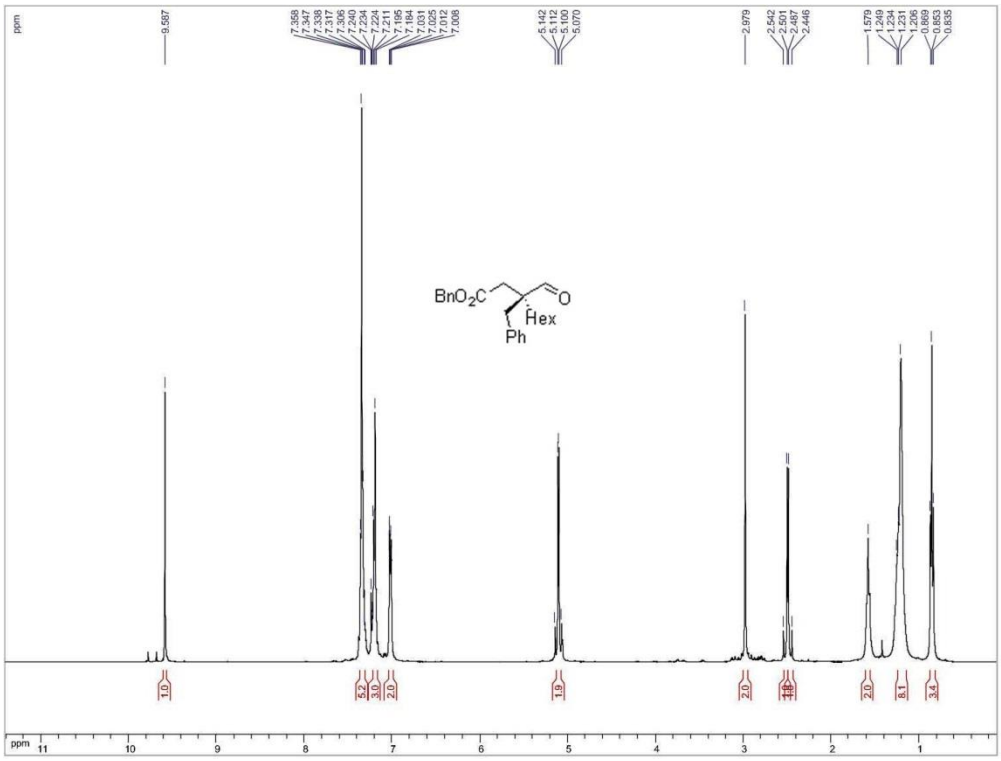

^{1}H NMR spectrum of 4h (400 MHz, $CDCl_3$):



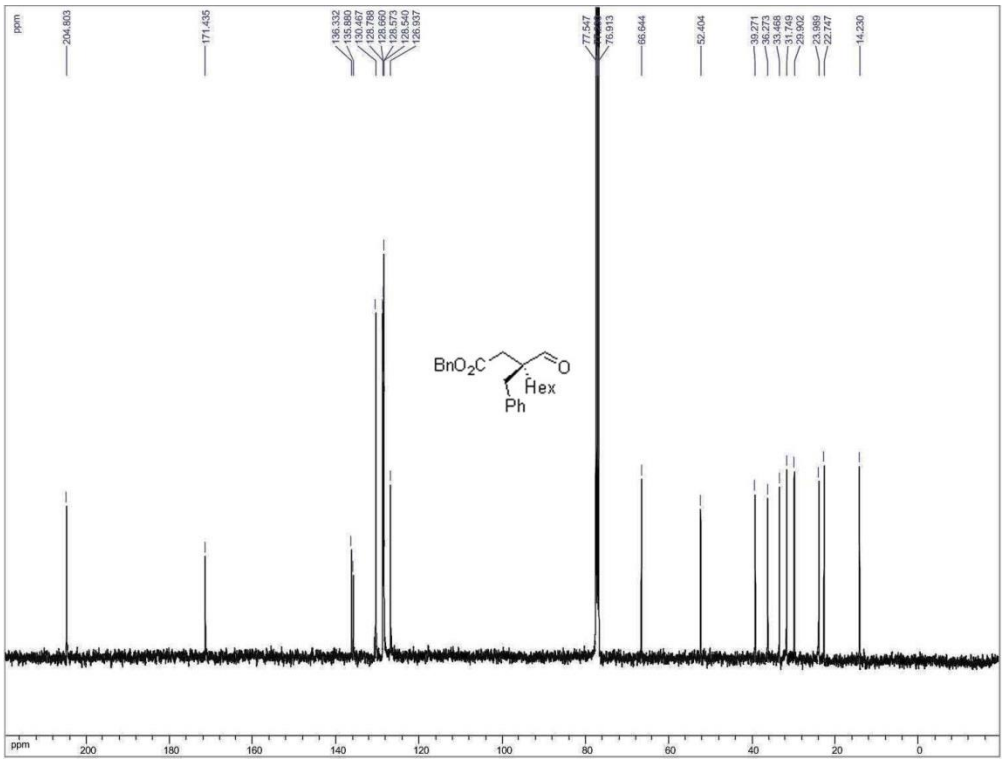
^{13}C NMR spectrum of 4h (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of 5h (400 MHz, $CDCl_3$):

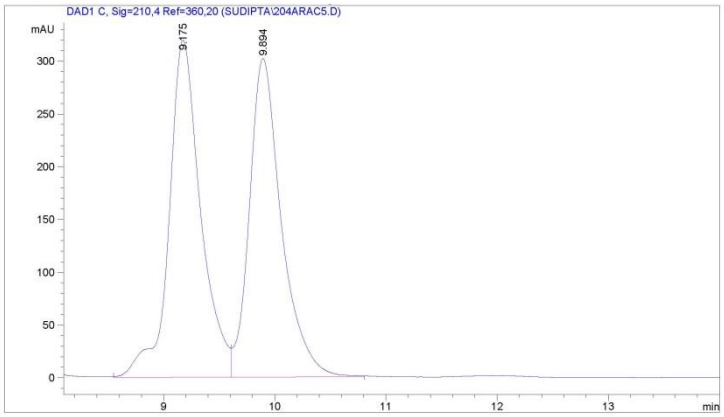


^{13}C NMR spectrum of 5h (100 MHz, $CDCl_3$):



HPLC analysis of the racemic and enantioenriched 5h:

OD
Hex/iPrOH = 99:1
1 mL/min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

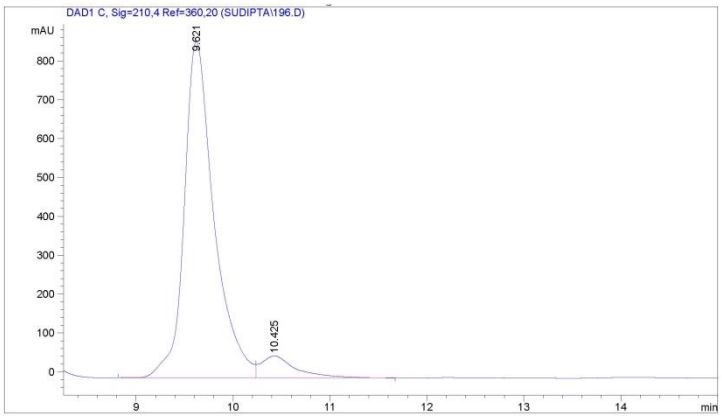
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.175	BV	0.2911	6324.08691	319.29410	51.1981
2	9.894	VB	0.2971	6028.11084	301.70654	48.8019

Totals : 1.23522e4 621.00064

Results obtained with enhanced integrator!

*** End of Report ***

OD
Hex/iPrOH = 99:1
1 mL/min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

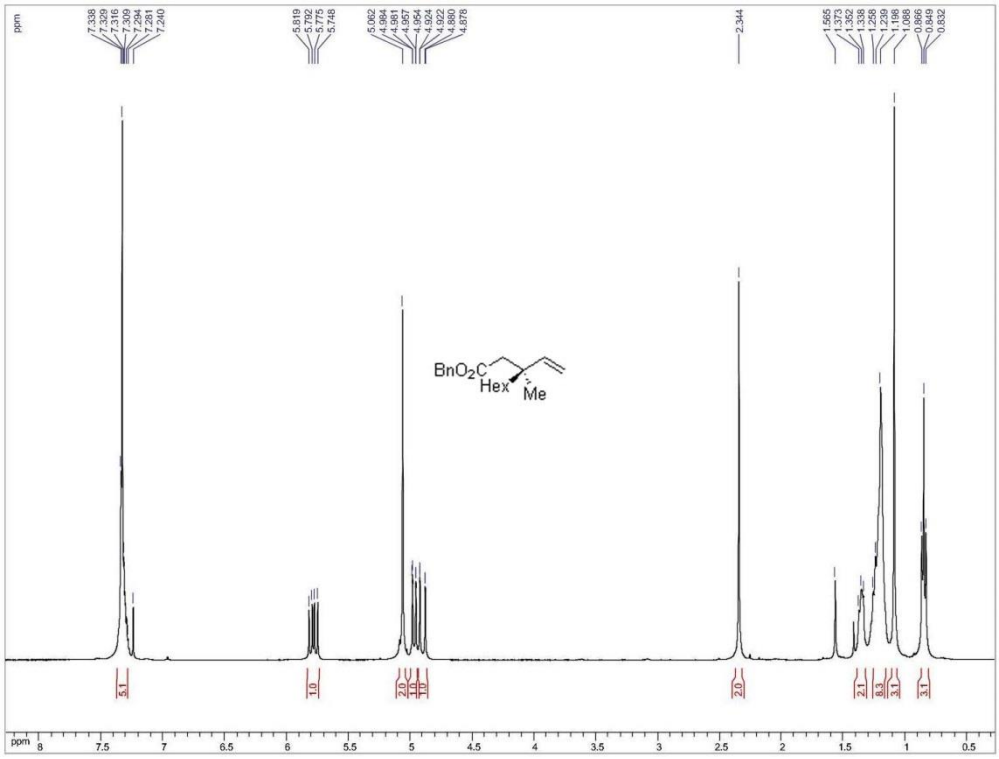
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.621	BV	0.3149	1.84658e4	865.60236	92.8655
2	10.425	VP	0.3530	1418.66406	56.87531	7.1345

Totals : 1.98845e4 922.47767

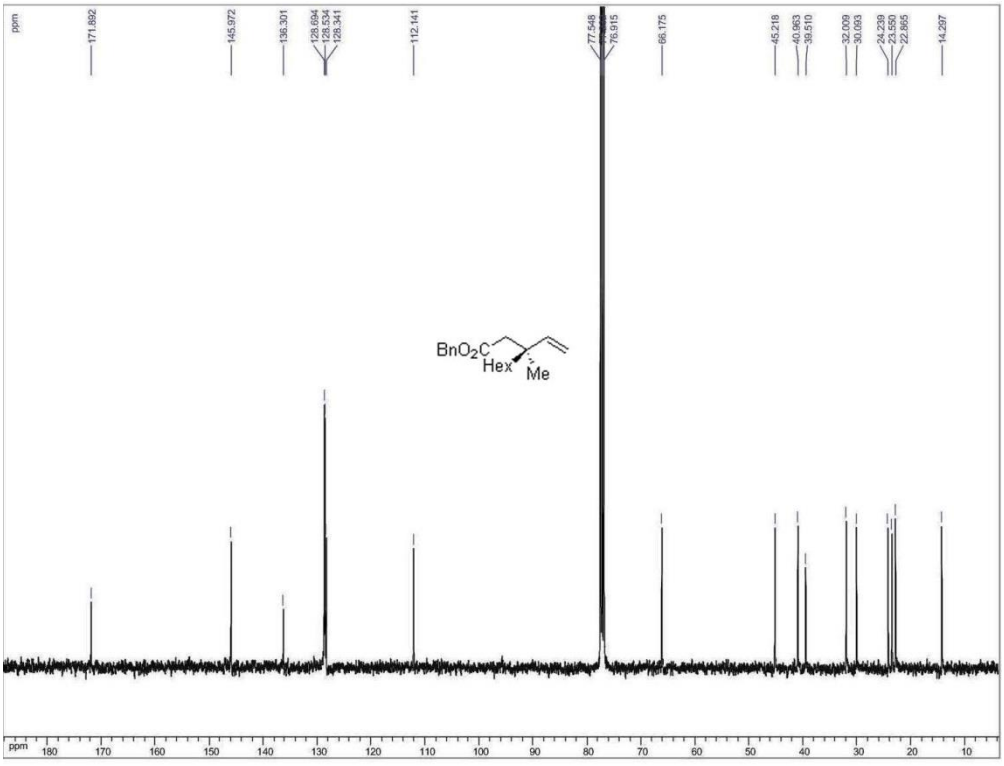
Results obtained with enhanced integrator!

*** End of Report ***

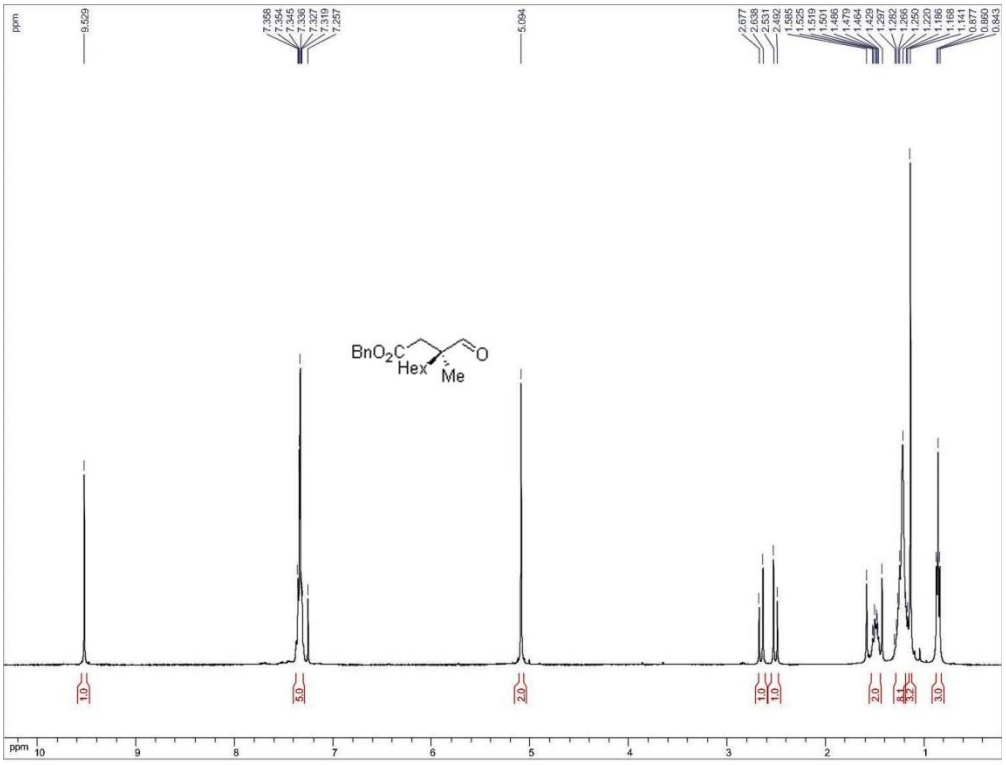
^{1}H NMR spectrum of 4i (400 MHz, $CDCl_3$):



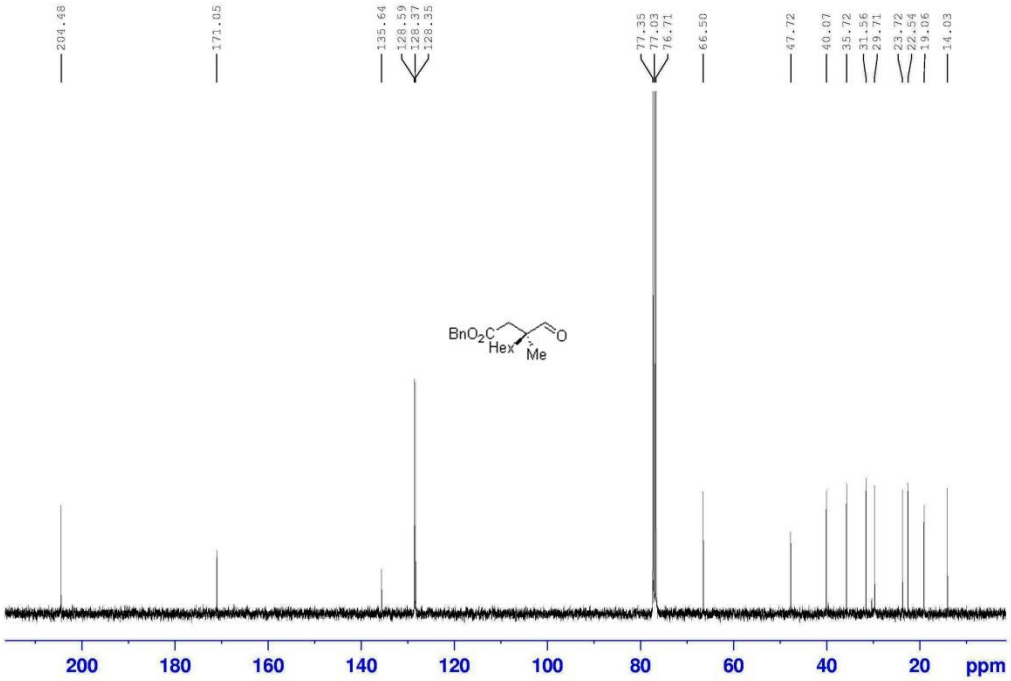
^{13}C NMR spectrum of 4i (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of 5i (400 MHz, $CDCl_3$):

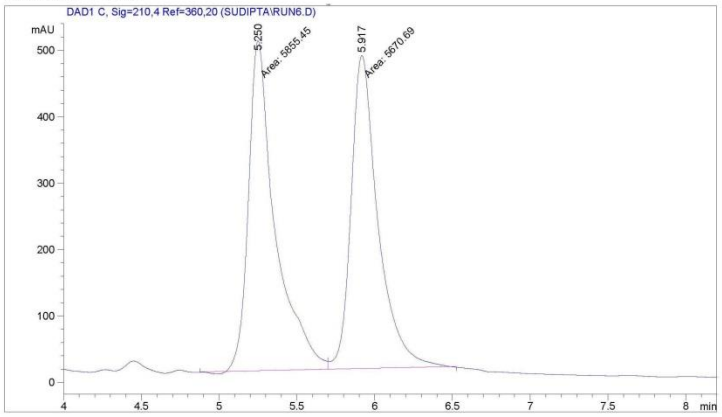


^{13}C NMR spectrum of 5i (100 MHz, $CDCl_3$):



HPLC analysis of the racemic and enantioenriched *S*-5i:

OD
1 ml/min
Hex:iPrOH = 90:10

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

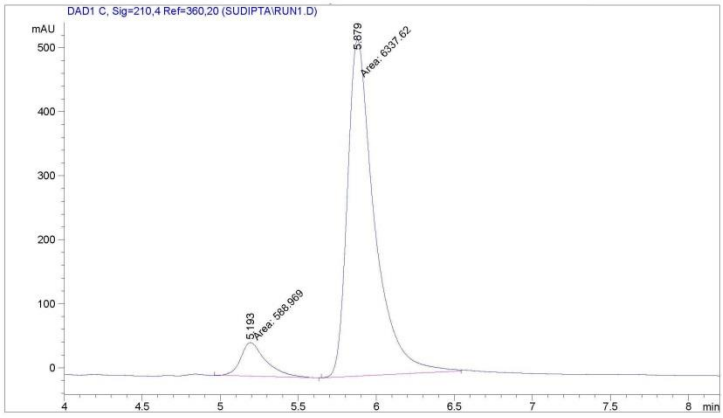

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.250 MF    0.1961 5855.44824  497.60339  50.8015
   2   5.917 FM    0.2003 5670.69434  471.85657  49.1985

Totals :                  1.15261e4   969.45996

 Results obtained with enhanced integrator!
=====================================================================
                      *** End of Report ***
```

OD
1 ml/min
Hex:iPrOH = 90:10

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.193 MM    0.1869  588.96869   52.51818   8.5030
   2   5.879 MM    0.2008 6337.62451  526.09332  91.4970

Totals :                  6926.59320  578.61150

 Results obtained with enhanced integrator!
=====================================================================
                      *** End of Report ***
```
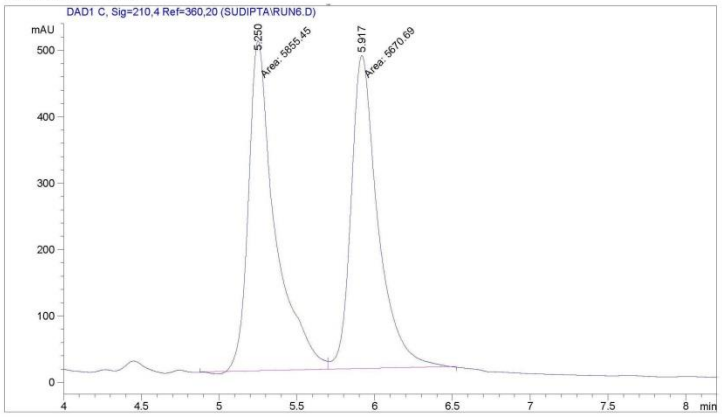

HPLC analysis of the racemic and enantioenriched *R*-5i:

OD
1 ml/min
Hex:iPrOH = 90:10

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

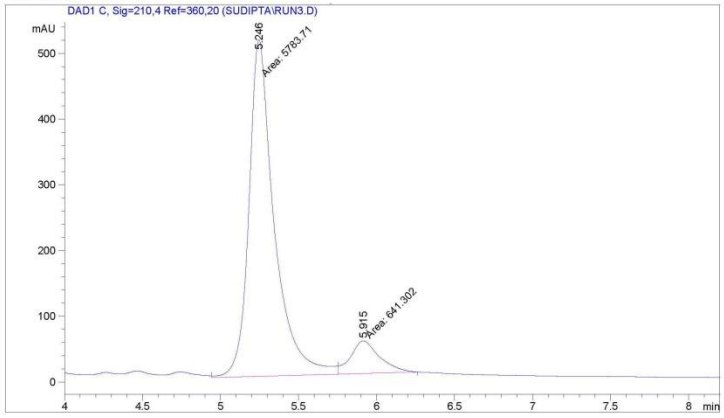

Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.250 MF    0.1961 5855.44824  497.60339  50.8015
   2   5.917 FM    0.2003 5670.69434  471.85657  49.1985

Totals :                  1.15261e4   969.45996

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

OD
1 ml/min
Hex:iPrOH = 90:10

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,4 Ref=360,20

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.246 MF    0.1880 5783.71289  512.81396  90.0187
   2   5.915 FM    0.2148  641.30164   49.75755   9.9813

Totals :                  6425.01453  562.57151

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```
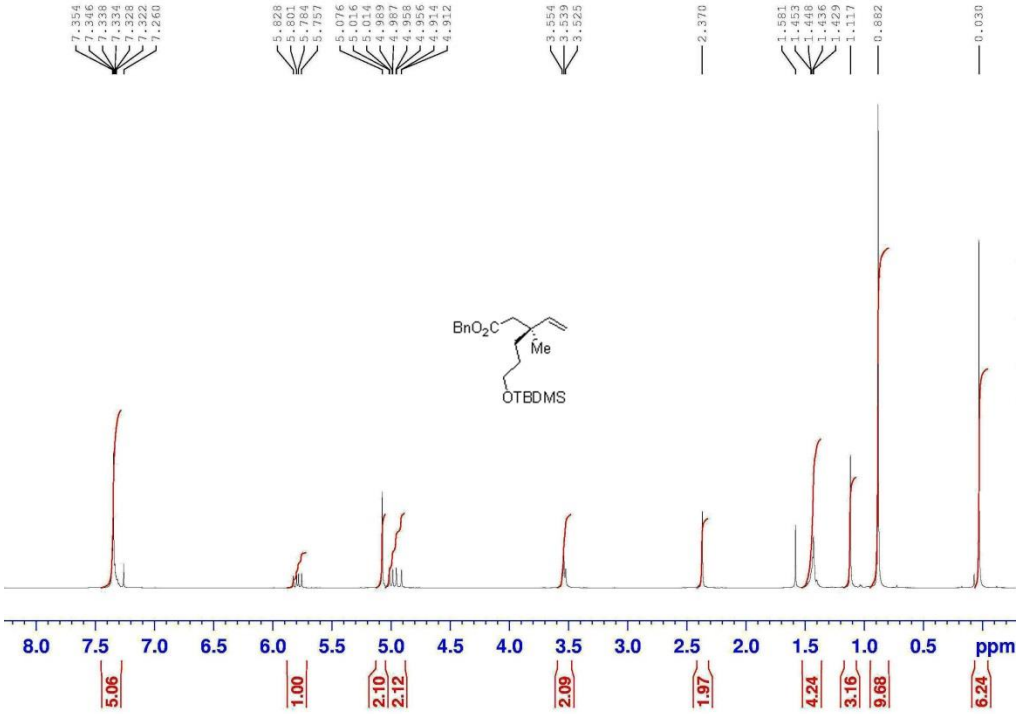
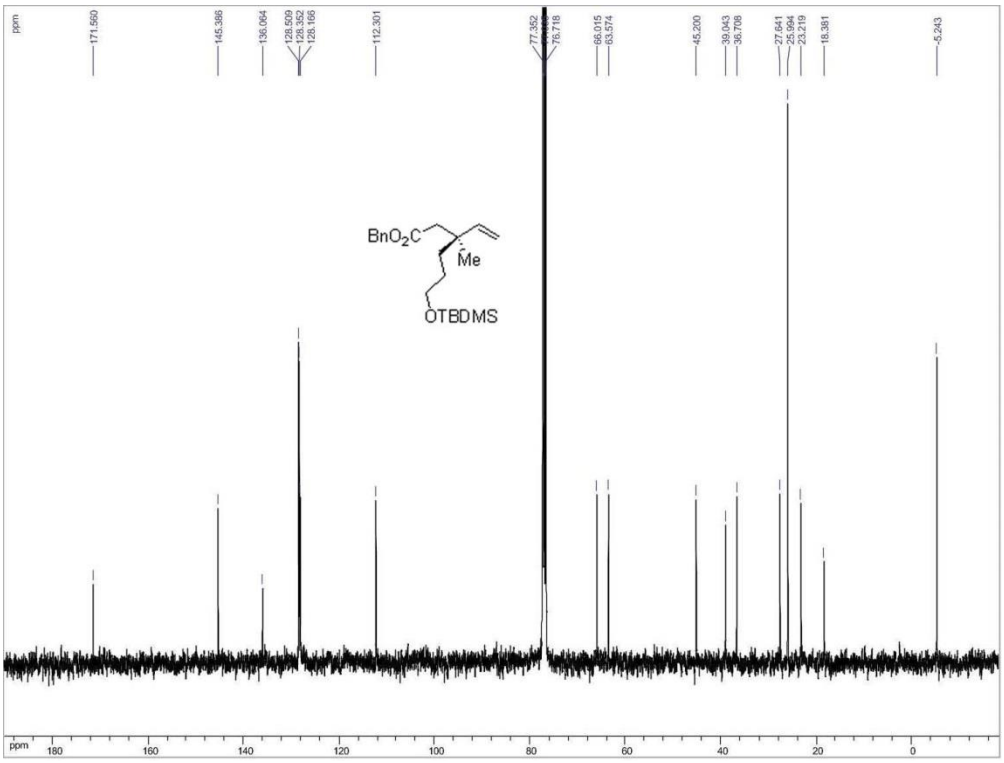
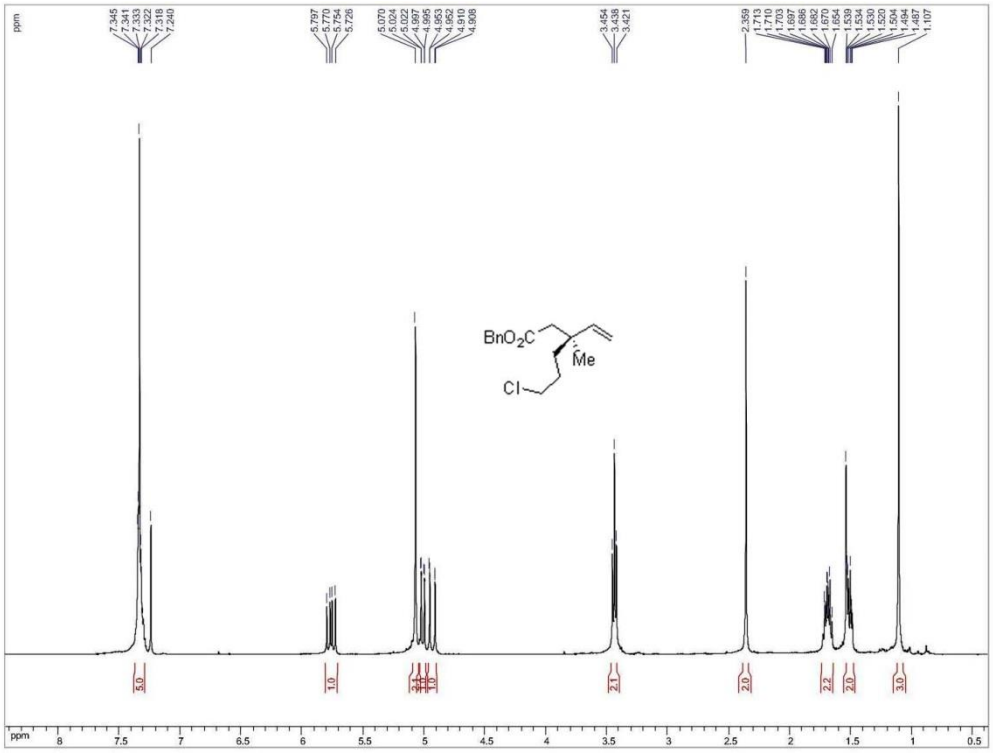

^{1}H NMR spectrum of 4j (400 MHz, $CDCl_3$):



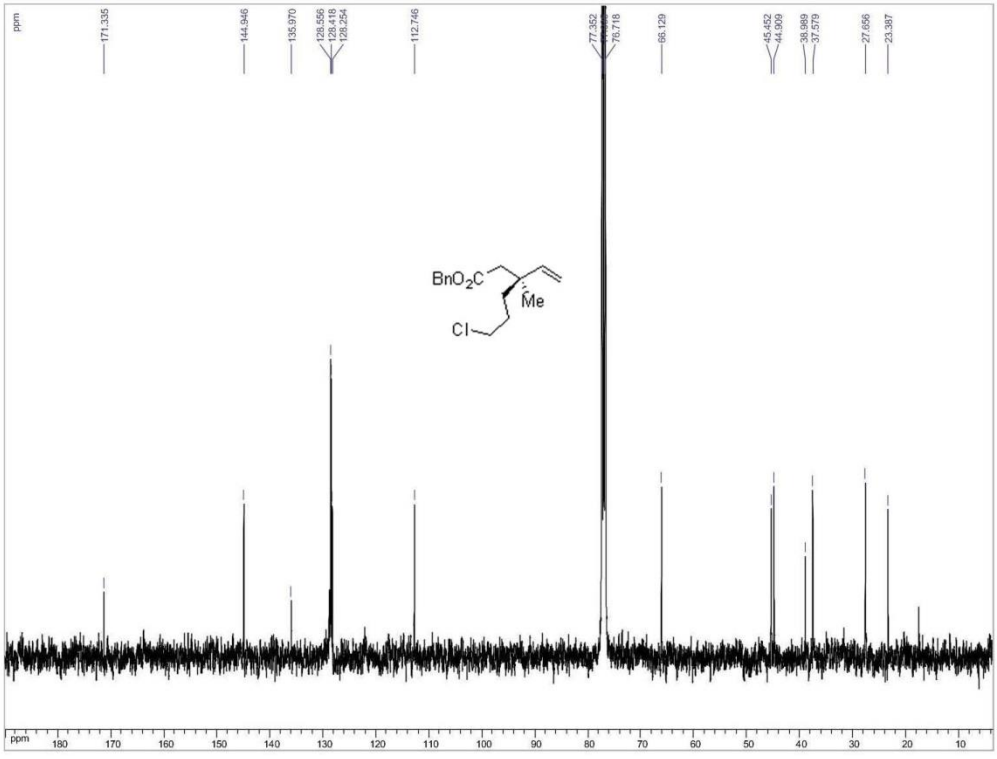
^{13}C NMR spectrum of 4j (100 MHz, $CDCl_3$):



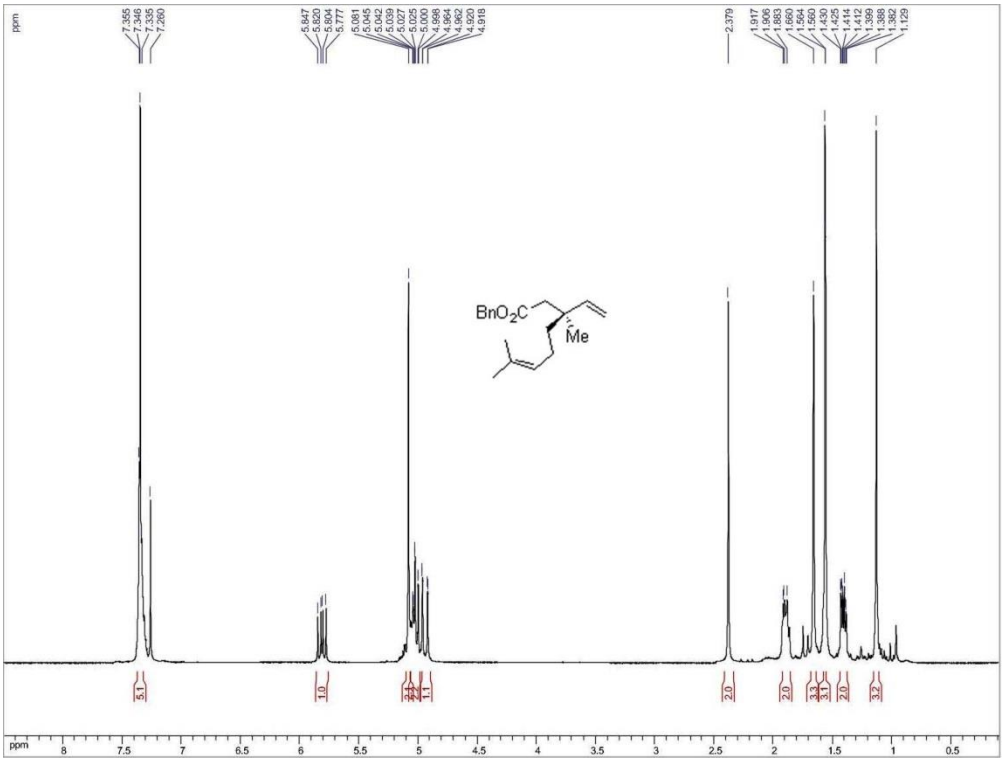
^{1}H NMR spectrum of 4k (400 MHz, $CDCl_3$):



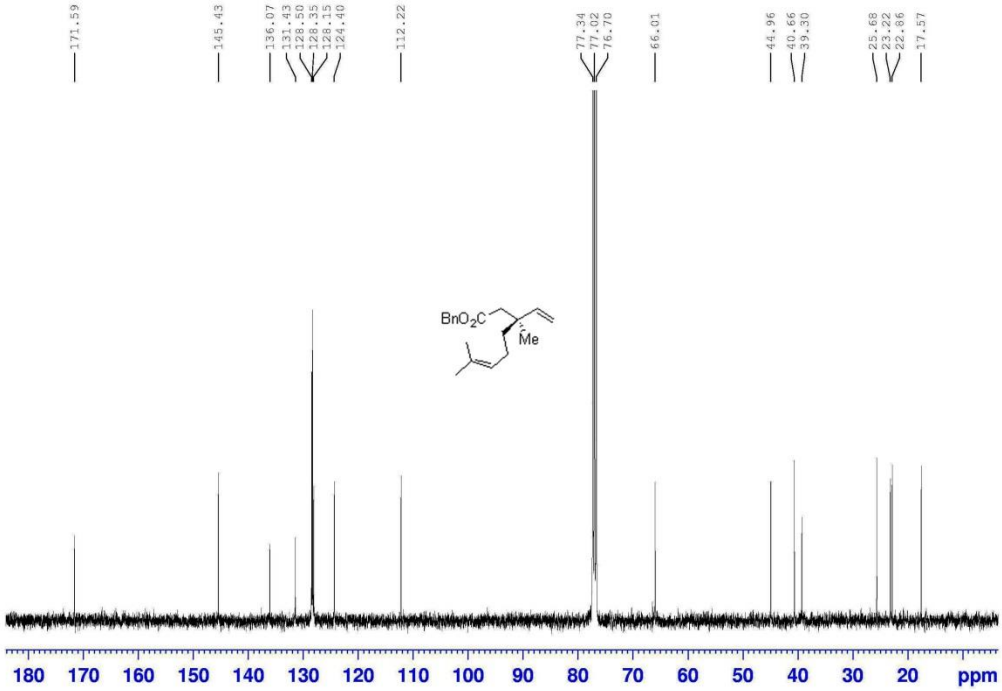
^{13}C NMR spectrum of 4k (100 MHz, $CDCl_3$):



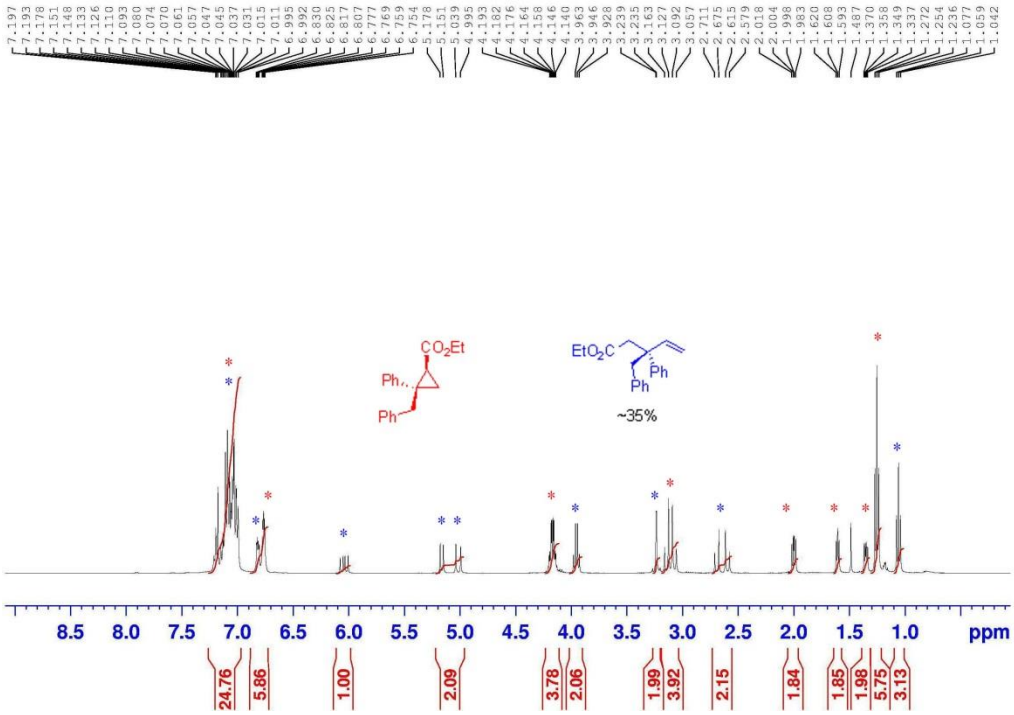
^{1}H NMR spectrum of 4l (400 MHz, $CDCl_3$):



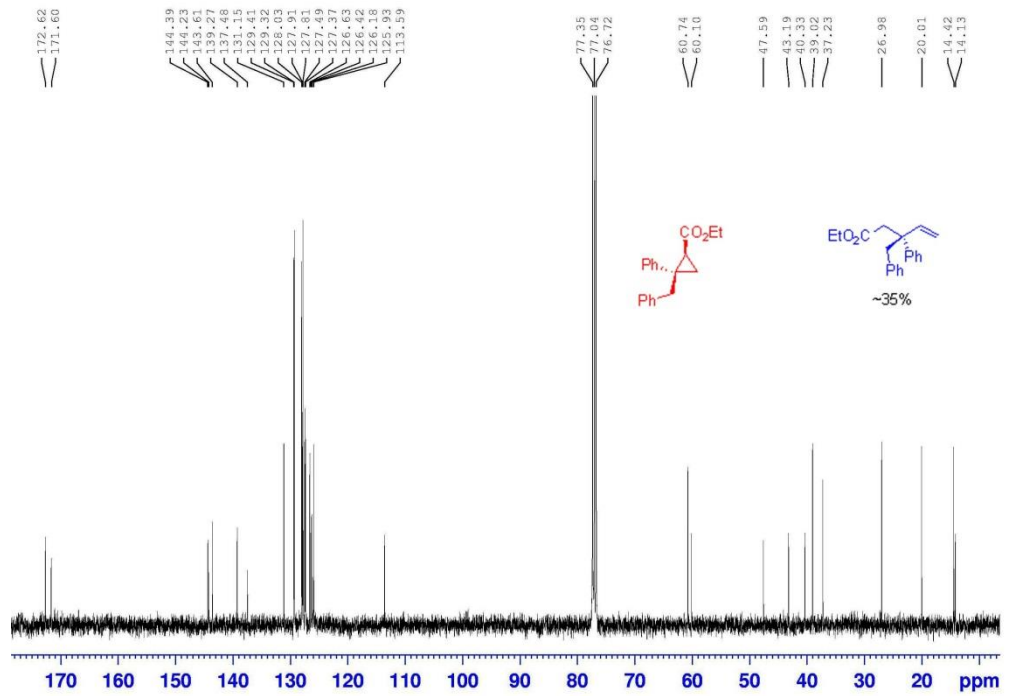
^{13}C NMR spectrum of 4l (100 MHz, $CDCl_3$):



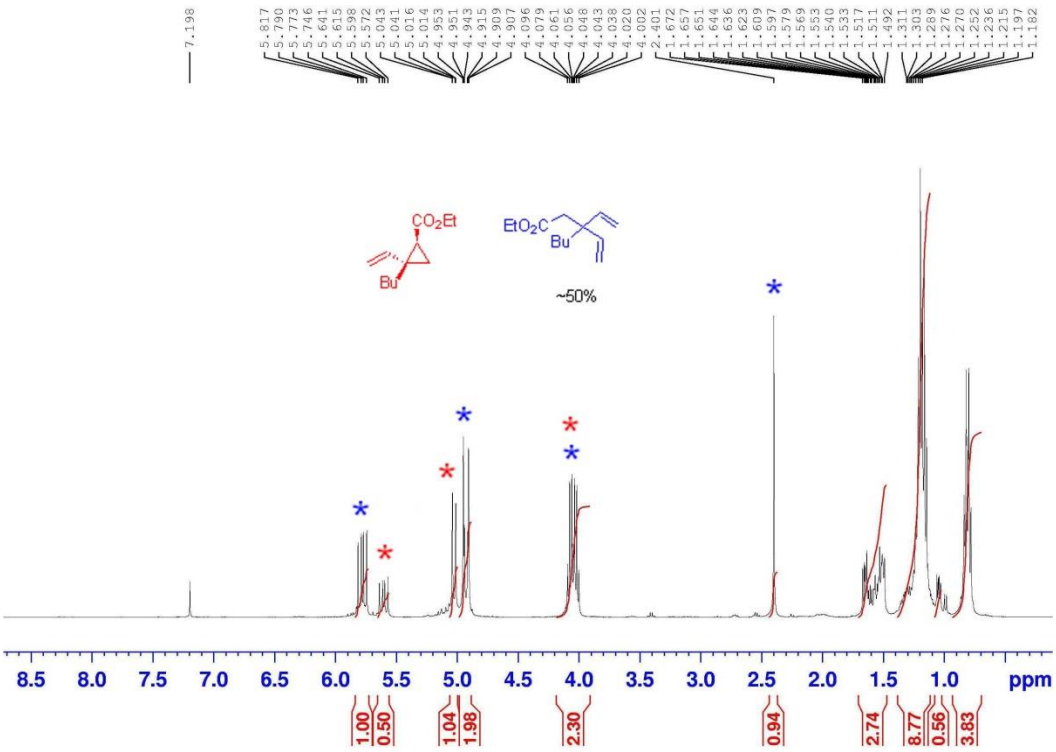
[1]H NMR spectrum for the reaction of 1d with PhLi for the formation of 4m:



[13]C NMR spectrum for the reaction of 1d with PhLi for the formation of 4m:



^{1}H NMR spectrum for the reaction of 1j with C_2H_3MgBr for the formation of 4n:



^{13}C NMR spectrum for the reaction of 1j with C_2H_3MgBr for the formation of 4n: